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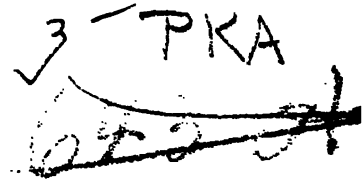
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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

WILLIAM FRANCIS, PH.D., F.L.S., F.R.A.S., F.C.S.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Fluorine Salts of Antimony. *By* F. A. Flückiger.

With regard to the correct application of the term salt chemists are still of different opinions. Lavoisier was acquainted only with oxygen salts, and put forward the principle that salts were quaternary compounds consisting of an acid and a base. When the true constitution of common salt was discovered, the great difference between it and the quaternary *oxygen salts* led Berzelius to apply to analogous binary compounds the name of *haloid salts*. Davy endeavoured to abolish this distinction by regarding all acids as binary hydrogen compounds; and although this view has many advantages, it involves the assumption of too great a number of hypothetical bodies of altogether unusual composition. A third view of the constitution of salts owes its first origin to Berzelius, who showed that sulphur combined on the one hand with very negative and on the other with very positive elements, furnishing two groups of sulphurets, bearing to each other the relation of acids and bases and forming quaternary *sulphur salts*. Selenium and tellurium behave in the same manner, and Berzelius called this third class of salts *amphide salts*.

The extension of this view to still more negative elements—chlorine, bromine and iodine—was natural, and they were declared by v. Bonsdorff* and P. Boullay† to be "*corpora amphigenia*," both of whom founded their opinions upon the investigation of a great number of iodine, chlorine and bromine compounds. These chemists thus returned to Lavoisier's definition, regarding quaternary compounds only as salts, the haloid compounds of Berzelius as acids or bases, and assigning to a whole group of negative elements a part in the formation of acids and bases similar to that which Lavoisier supposed peculiar to oxygen. Berzelius, however, still adhered to his own views; he would not recognise the analogy between quaternary, chlorine, bromine, and iodine compounds and his

* Poggendorff's Annalen, xvii. 115.

† Ann. de Chim. et de Phys., xxiv. p. 337.

amphide salts, and the existence of binary as well as quaternary salts was maintained by him and his school.

One objection* which was made to v. Bonsdorff's views was, that he had not obtained any compounds of the most negative with the most positive chlorides. Considering the very little attention which chemists have paid to this question, it is not to be wondered at that all the possible compounds of this kind have not been obtained; still a sufficient number are known to destroy this objection, for instance $SbCl^5+3SCl^2$† and $SnCl^2+2SCl^2$ (H. Rose‡), $Hg^2Cl+SCl$ (Capitaine§), $KCl+ICl^3$ and $AmCl+ICl^3$ (Filhol‖), $KCl+O^5Cl^2$, and a fluotelluride of sodium not yet analysed (Berzelius).

It is certainly desirable that the compounds of elements between the extremes of the electro-chemical scale should be examined.

Another objection brought forward by H. Rose¶, in especial reference to the chloro-hydrargyrates, is the circumstance that oxide of mercury presents no acid characters, whence it must be inferred that the corresponding chloride is not an acid. Independent of the reddening of litmus by this chloride, it may be remarked, in answer to this objection, that we are not justified in supposing that there is a perfect parallelism in the relative acid and basic characters of the chlorine, bromine, or iodine compounds and the oxides. The solubility of the bodies must be taken into account. A proof of the non-existence of such a parallelism is furnished by the compound $KS+HgS+5HO$ (Brunner**), which must undoubtedly be regarded as a sulphur salt as much as any one obtained by Berzelius.

The large number of quaternary fluorine compounds examined by Berzelius†† were regarded by him as double haloid salts, and by v. Bonsdorff‡‡ as quaternary fluorine salts. H. Rose§§, in other respects adhering to the views of Berzelius, admitted that, in consequence of the great analogy between these fluorine compounds and the sulphur salts, the former might fairly be regarded as fluorine salts in v. Bonsdorff's sense of the term. Fluorine seems then as if it were destined to decide the dispute. If the supporters of the haloid theory acknowledge the existence of fluorine salts to be admissible, it devolves upon the supporters of the opposite view to prove that their analogy with the quaternary chlorine, bromine, and iodine compounds is still greater than with the sulphur salts; and therefore admitting the existence of fluorine salts, the existence of chlorine, bromine, and iodine salts in v. Bonsdorff's sense follows as a necessary consequence. The fact that this analogy between quaternary fluorine and chlorine compounds has hitherto been overlooked, is solely owing to the want of evidence, for no truly corresponding compounds of fluorine and chlorine‖‖ have been made known. More-

* Poggendorff's Annalen, xvii. † *Ib.*, xlii. p. 532. ‡ *Ib.*, 517.
§ Journ. der Pharm., xxv. ‖ *Ib.* ¶ Poggendorff's Annalen, lv. 552.
** *Ib.*, xv. 596. †† *Ib.*, i. 2, 4.
‡‡ *Ib.*, xix. 348. §§ *Ib.*, lv. 537.
‖‖ The only example, and that not of strict correspondence, which could be brought forward is presented by the bodies $3AmCl+2TiCl^2$ (Rose), $AmF+TiF^2$ and $AmF+2TiF^2$, examined but not analysed by Berzelius.

over, the authority of Berzelius contributed to the same result, inasmuch as he simply ignored the arguments of v. Bonsdorff.

Being convinced of the correctness of v. Bonsdorff's views, it seemed to me desirable to furnish some further confirmation of them. For this purpose two methods might be adopted,—the preparation of chlorine compounds corresponding to the fluorine salts of Berzelius, or of fluorine compounds corresponding to the already known chlorine compounds. The latter course was chosen, because it would at the same time enlarge our imperfect knowledge of fluorine.

The only electro-negative element which could be selected as capable of furnishing fluorine compounds playing the part of acids was antimony, because fluorides of chlorine, bromine, iodine, and perhaps sulphur or phosphorus, do not appear to exist, and because it is the only electro-negative element whose chlorine salts have been examined.

Fluoride of antimony was investigated by Berzelius in 1824. He found that oxide of antimony dissolved in hydrofluoric acid, forming a crystalline compound readily soluble in water without decomposition. He stated, further, that fluoride of antimony combined with alkaline fluorides, forming what he regarded as double salts, which were less soluble than those of uranium or the individual fluorides of which they consisted, but were still crystallizable. It seems, consequently, that Berzelius did not examine any of these salts more closely; indeed, from what he says of their solubility, it might almost be conjectured that he did not really prepare any of them.

Dumas prepared fluoride of antimony in 1826 by distilling fluoride of mercury with antimony. He states that it is solid at the ordinary temperature, snow-white, has a volatility between that of water and anhydrous sulphuric acid, and a composition corresponding to the chloride and oxide. Neither Berzelius nor Dumas made any quantitative examination of the body, judging from analogy that there could be no doubt as to the relation of fluorine to antimony. Still it was remarkable that Berzelius should mention the compounds SbF^4 and SbF^5 in his 'Lehrbuch,' and ascribe to them the same characters as SbF^3, especially the capability of combining with the more positive fluorides. A further examination of the compounds of fluorine with antimony was therefore desirable.

Fluoride of antimony is best prepared by dissolving the oxide in hydrofluoric acid. Metallic antimony is not acted upon more strongly by the most concentrated hydrofluoric acid than by hydrochloric acid. Nor is it formed by the distillation of fluor-spar, antimony or its oxide and sulphuric acid. The distillate contains but traces of antimony; and when the metal is used, a large quantity of sulphurous acid passes over, and sulphur sublimes in the neck of the platinum retort. The distillation of fluoride of mercury with antimony is not an advisable method. On the contrary, oxide of antimony dissolves very readily in tolerably concentrated hydrofluoric acid with a most intense evolution of heat. On evaporating the liquid containing an excess of acid at 158° or 194° F., colourless trans-

parent crystals are obtained. Their size is inconsiderable, their form a regular octohedron of the rhombic system, perfectly corresponding to the crystals of the melted chloride. The crystals were not so perfect* as those of the chloride, most of them being hexagonal tables, a combination of the extremely truncated octohedron with a rhombic prism, in which the octohedral planes are sometimes entirely wanting. $SbCl^3$ presents similar hexagonal tables, except that the rhombic prism is in this case sharper. When a solution of fluoride of antimony is rapidly evaporated, prisms are formed, and when very rapidly with a constant excess of acid, small scales are formed. Neither the concentrated solution nor the salt itself smokes in the air. The crystals are so extremely deliquescent, that they cannot be dried. The salt is very acid, and afterwards styptic to the taste. It dissolves freely in water, and the solution is miscible in all proportions with water without becoming turbid, although when evaporated without maintaining a continual excess of acid, an insoluble powder separates (probably oxyfluoride), which redissolves on the addition of hydrofluoric or hydrochloric acid. The deliquescing crystals suffer the same change, giving off acid. I could not observe that this body was so volatile as Dumas states. Heated in the air, it gives off thick white vapours, but a portion of oxide of antimony always remains on the platinum spoon. On attempting to distil the salt after it had been rapidly pressed between bibulous paper, nothing passed over even at a red heat. In the neck of the retort there were thick, hard, deliquescent crusts with delicate brilliant needles pointing inwards, and at the bottom of the retort there was a quantity of oxide of antimony. It appears therefore that the dry fluoride of antimony is only partially volatile when heated with access of air†, probably in consequence of the formation of hydrofluoric acid from a part of the fluoride. The extreme tendency of fluorine to assume the gaseous state and combine with hydrogen may perhaps be the reason why the fluoride of antimony has no great stability, although it appears to be a more intimate combination than the chloride. These characters appeared to render an accurate direct analysis impracticable. However, a quantity of small crystals, dried as rapidly and thoroughly as possible, were weighed, decomposed by sulphuric acid (hydrofluoric acid was not disengaged until heat was applied), and then treated with sulphuretted hydrogen. The sulphuret of antimony, dried at 212° F., corresponded to 68·38 per cent. of antimony. Theory requires—

Antimony	68·38	1 =	129·0	69·69
Fluorine	..	3	56·1	30·31

There can consequently be no doubt that the compound is SbF^3. The loss of fluorine and absorption of oxygen on exposure to the air was proved as follows. Tolerably well-formed prismatic crystals were pressed between bibulous paper until they appeared in some degree dry. They then gave—

* This was probably owing to the small quantities of material with which it was necessary to operate.

† The platinum retort employed was tolerably capacious.

Antimony	75·12	75·66	2 =	258·0	76·30
Fluorine	15·09	..	3	56·1	16·60
Oxygen	..	..	3	24·0	7·10

It does not however appear certain that the substance analysed was an oxyfluoride of definite composition. It is perhaps more probable that the decomposition goes on until all the fluorine is separated. However, the oxyfluoride does not deliquesce after it has been dried between paper, and it likewise appears to be formed when an excess of oxide of antimony is added to hydrofluoric acid.

It is much to be regretted that Berzelius has nowhere described the preparation of the two fluorides SbF^4 and SbF^5. The existence of the former will certainly no longer be admitted, and it was perhaps inferred by Berzelius solely from a supposed analogy with SbO^4, which is no longer regarded as a binary compound. On the contrary, judging from the analogy between fluorine and chlorine, it must be admitted as highly probable that antimony combines with 5 equivs. of fluorine, though the instability of SbF^3 is certainly calculated to excite doubt. The following attempt was made to prepare SbF^5. Anhydrous antimonic acid, prepared by means of nitric acid, treated with concentrated hydrofluoric acid, was not dissolved. Hydrated antimonic acid, precipitated by nitric acid from antimoniate of potash, was apparently dissolved by nitric acid with evolution of heat. The solution was however only apparent, for filtration separated a transparent gelatinous mass of antimonic acid, and the filtrate contained only traces of antimony. The evolution of heat was a consequence of the combination of hydrofluoric acid with the water of the antimonic acid. On treating a mixture of 3 equivs. of carbonate of potash and 1 equiv. of hydrated antimonic acid with concentrated hydrofluoric acid, boiling and filtering in order to effect the combination of 1 equiv. of antimony with 5 equivs. of fluorine by predisposing affinity, and to obtain the salt $3KF + SbF^5$, the antimonic acid remained upon the filter; while deliquescent fluoride of potassium crystallized from the filtrate. Antimonic acid, distilled with fluor-spar and sulphuric acid, did not yield SbF^3, nor was SbF^5 formed on heating antimonic acid with dry fluoride of mercury in a platinum retort. It may be inferred from these negative results, that SbF^5 does not exist any more than SbF^4.

Fluoantimoniate of Fluoride of Potassium.—The above preliminary experiments having led to a more accurate knowledge of the fluoantimonic acid, the proper object of the investigation was again pursued, and a potassium salt first prepared. It appeared *à priori* most probable, that if these salts really existed, they would have a composition agreeing with the formula $3RF + SbF^3$, for which the proportion of oxide of antimony to carbonate of potash is as 163 to 200. The former substance was made into a paste with water dissolved in excess of hydrofluoric acid, and the liquid so far saturated with carbonate of potash as to leave some excess of acid. The solution was then filtered upon a silver funnel, and exposed to a temperature of 32° F. in a platinum dish. In a short time small laminæ crystallized out in such quantity that the whole mass appeared pasty.

However, this appearance is very deceptive, for from the way in which the crystals are arranged an immense quantity of mother-liquor is enclosed between them. On recrystallization and gradual cooling, the salt assumed the form of very thin, transparent, rectangular laminæ, remarkably similar to those of naphthaline crystallized from alcohol, although the latter are rhombic plates. They are obtained most perfect by evaporating a saturated solution at 140° or 158° F. The salt retains its acid reaction even after repeated crystallization; to the taste it is at first pleasantly acid, but afterwards styptic; 1 part dissolves in 9 parts of water at 55°·4 F., and in somewhat less than twice its weight of boiling water, the solution solidifying upon cooling. It is insoluble in alcohol and æther, both of which precipitate it from a saturated or dilute aqueous solution in a flocculent form. When concentrated sulphuric acid is poured upon the crystals, they immediately lose their transparency, and a part of the fluorine is disengaged as hydrofluoric acid, with elevation of temperature, but no effervescence. Even on applying heat, it is long before all the fluorine is separated, and still longer when concentrated hydrochloric acid in great excess is used instead of sulphuric. Heated to 248° F., the salt does not decrease in weight; at a higher temperature, though below that of a red heat, visible by daylight, it melts quickly, and loses only 0·8 or 1·6 per cent. in a closed platinum crucible; on cooling, it solidifies to a crystalline lamellar mass. Heated in an open crucible, it is decomposed at a very high temperature. The loss is from 9 to 14 per cent., according as the temperature is raised gradually or suddenly. The atomic weight of the salt is ..... 302·5

Assuming that upon heating it all the fluorine combined with antimony is separated.... = 56·1

246·4

and that the antimony combines with 3 equivs. of oxygen..... = 24·0

the residue should amount to ..... 270·1 = 10·6 per cent.

If however at first either some SbF^3 or undecomposed salt is volatilized, the observed loss on ignition may easily be accounted for. The alkaline reaction of the residue left on ignition is probably owing to the formation of neutral fluoride of potassium. If the salt is carefully dried and preserved in well-closed glass vessels, the glass is not acted upon* except when a trace of moisture is present. Very smooth glass is less acted upon than rough. The solution of the salt acts upon glass strongly during spontaneous evaporation. Zinc and tin precipitate antimony from the solution, but not completely even after a long time and with addition of hydrochloric or sulphuric acid, at least when platinum vessels are used, so that the antimony cannot be determined in this way. The analysis was therefore conducted by first separating the fluorine from a weighed quantity by heating with sulphuric acid, so that the subsequent operations could

* As far as I could judge during the lapse of four months.

be carried on in glass vessels. In order to separate the fluorine completely from only 1 grm. of the salt, it was necessary to use a large excess of concentrated sulphuric acid, and to apply a strong heat for some hours in a sand-bath. After the separation was effected, the residue was diluted with water (generally attended with precipitation of oxide of antimony or a basic salt), and all the antimony precipitated by sulphuretted hydrogen. The sulphuret was collected on a weighed filter, dried at 212° F., and weighed, oxidized by means of nitrohydrochloric acid, and the per-centage of sulphur determined. The quantity of sulphuret of antimony, minus the sulphur of the sulphate of baryta, gave the per-centage of antimony*. This mode of estimating the antimony was chosen because the reduction of the sulphuret by means of hydrogen is troublesome and less trustworthy. The potash was estimated in the usual way in the liquid filtered from the sulphuret of antimony, and the fluorine as fluoride of calcium with a fresh quantity of the salt. When the pure solution of this, or one of the following salts, was treated with chloride of calcium, basic chloride of antimony separated from the filtrate in very beautiful crystals. It was therefore necessary to separate the fluoride of calcium rapidly, or previously to add tartaric acid to the solution. The neglect of this precaution will account for the excess of fluorine in one of the following analyses. Two analyses of this salt gave in 100 parts—

Potassium	27·78	27·18	2	26·45
Antimony.....	41·71	41·60	1	42·64
Fluorine	30·41	32·89	5	30·91

which give the formula $2KF+SbF^3$. The corresponding chlorine salt is $2KCl+SbCl^3$ (Jacquelain)†, which crystallizes in oblique rhombic prisms.

Sometimes, when a recently-prepared solution of the salt is allowed to crystallize, small pointed octohedrons or rhombic plates separate instead of the usual tabular crystals. If the crystallization is allowed to proceed for some days, the liquid gradually becomes turbid, the crystals lose their transparency, and are covered with a white powder. If the liquid is then somewhat diluted, hydrofluoric acid added and warmed, the whole becomes clear, and the usual rectangular tables are then deposited. I was unable to ascertain the conditions under which this octohedral salt is formed. The analysis gave—

Potassium	27·45
Antimony	41·40

It is anhydrous, and notwithstanding the apparently different form, must be the same salt. Its solubility is the same, and it assumes

* In some of the following analyses this precaution was not taken, but the sulphuret determined directly as SbS^3, since in the most unfavourable instances, when a very acid solution was very slowly precipitated by sulphuretted hydrogen, the calculated quantity of antimony was only at the most from 1·5 to 2·0 per cent. too high.

† Ann. de Chim. et de Phys., lxvi.

the rectangular form when dissolved in water and crystallized between 104° and 122° F.

It has already been mentioned, that the compound $3KF+SbF^3$ was sought and the substances mixed in such proportions. However, as the salt $2KF+SbF^3$ was formed, it would appear that, at least with respect to KF, the acid SbF^3 has a greater tendency to combine with 2 equivs. of base. The same remark appears to apply to the corresponding chlorine salts*. It is probable that $3KF+SbF^3$ might be obtained, although this was not attempted, as a sodium salt furnished a good example of a tribasic fluorine salt. On the contrary, it was desirable to try whether salts having the formula $RF+SbF^3$ could be obtained, and this was effected by treating a mixture of SbO^3 and KO,CO^2 in suitable proportions with HF. The warm saturated solution gave on cooling, large hard octohedrons, which became opake in the air. When the solution cooled slowly, delicate silky needles were formed, sometimes grouped together like wavellite, at others like loose asbestos, and enclosing a great deal of mother-liquor. The octohedrons belong to the rhombic system, and are combined with a rhombic prism of the same order†.

Secondary planes are unfrequent and indistinct. The salt suffers no loss of weight at 212° F., and is therefore anhydrous. It is more soluble than the former, 1 part requiring only $2\frac{3}{4}$ parts of water for solution. Well-formed octohedrons, such as were formed at the first, could not be obtained again on subsequent crystallization, but only the acicular crystals. Analysis gave—

	Octohedrons.	Needles.		
Potassium	15·62	14·50	1	16·40
Antimony.....	52·58	53·66	1	52·93
Fluorine	..	..	4	30·67

The corresponding chlorine salt is not known, and I was unsuccessful in an attempt to obtain it.

Fluoantimoniate of Fluoride of Sodium.—In order to obtain the salt $3NaF+SbF^3$, 153 parts SbO^3 were dissolved in excess of HF, and 126 parts NaF added. Upon the cooling of the hot saturated solution, small and extremely brilliant transparent prisms were formed between granular particles of the salt. Even when a large quantity of the solution is slowly evaporated, these prisms never attain a greater length than 0·003 millim., and the thickness is always less than 0·001 millim. Examined by the microscope, they proved to be rhombic prisms, very rarely modified by domatic planes. This simple form presents itself with remarkable regularity. The general behaviour of the salt is the same as that of the first potassium salt; it requires, however, 14 parts of water for solution at the ordinary temperature, and not less than 4 parts at 212° F. The solution is acid to the taste and litmus. It requires a somewhat higher temperature for fusion, which is quiet but accompanied by decomposition. Carefully melted in a closed platinum crucible, the

* Jacquelain, Ann. de Chim. et de Phys., lxvi.

† For these data I am indebted to Prof. Delffs.

salt lost 5·8 per cent. The fusion is moreover less decided, and on cooling the mass contracts greatly without presenting the fine lamellar texture of the potassium salt. Ignited in an open crucible, about one-half remains, fluoride of antimony being disengaged. Nitrohydrochloric acid extracts a little antimony from the alkaline residue. This salt is anhydrous; it is slowly decomposed by sulphuric acid without effervescence. The analysis did not at first give definite results, perhaps because the granular salt had a composition different from that of the prisms. The recrystallized salt, consisting almost entirely of prisms, gave—

Sodium	22·84	22·94	3	22·39
Fluorine	..	..	6	36·11
Antimony	38·40	..	5	41·50

Consequently the formula is, as was expected, $3NaF+SbF^3$. The discrepancy in the per-centage of antimony is owing to the above-mentioned circumstance. The corresponding chlorine salt $3NaCl+SbCl^3$ (Poggiale)*, crystallizes in laminæ.

Fluoantimoniate of Fluoride of Lithium.—The salt $2LF+SbF^3$ was obtained. It crystallized with great difficulty in large anhydrous prisms of indistinct figure, requiring more than 20 parts of water for solution:—

Lithium.....	4·10	2	5·44
Fluorine	..	5	39·75
Antimony.....	55·25	1	54·81

This salt was not further examined. No corresponding chlorine salt has been analysed.

Fluoantimoniate of Fluoride of Ammonium.—The salt $2AmF+SbF^3$ was obtained, although the substances were mixed in proportions corresponding with the tribasic formula. It crystallized in large rhombic tables and prisms belonging to the rhombic system. This salt is anhydrous, but attracts moisture from the air. It dissolves in 0·902 part of water, with considerable diminution of temperature, not so great however as in the case of chloride of ammonium. 7 grms. of the fluorine salt and 7 grms. of water at 63°·5 F. gave a temperature of 50°·9 F., while an equal quantity of water saturated with chloride of ammonium gives 42°·8 F. The aqueous solution tastes very acid, attacks glass strongly, and gives a flocculent precipitate with alcohol and æther. Sulphuric acid decomposes the salt with considerable elevation of temperature and effervescence. At 284° F. it does not lose ammonia, though when long exposed to the air it appears to decompose, as it is then only partly soluble in water, without addition of hydrofluoric acid. It is infusible; AmF sublimes when slowly heated, and some oxide of antimony remains; when heated very suddenly in a platinum crucible, it may be entirely volatilized, ammoniacal vapours escaping at the first. When the dry salt is rubbed with carefully-dried sodium, a feeble detonation is produced by strong pressure; and if water is added when

* Comptes Rendus, xx.

the decomposition has ended, and the mass washed with hydrochloric acid, black flocks of antimony remain. If the salt is wrapped in a sheet of sodium, laid upon a hard surface, and struck forcibly with a hammer, a very violent explosion takes place, but the decomposition is not complete. The above-described salts of potassium, sodium and lithium behave in a similar manner. Two analyses of this salt gave—

Ammonium		2	13·92
Fluorine		5	36·18
Antimony.....	48·10	1	49·90

This salt cannot be preserved in glass vessels so well as the potassium salt. Jacquelain* has examined the corresponding chlorine salt, $2AmCl+SbC^3$, which crystallizes in forms belonging to the hexagonal system (*dodécaèdres dérivés du prisme hexaèdre à six faces*). Poggiale† prepared a hydrated salt, $2AmCl+SbCl^3+2HO$, which, as he states, crystallizes in "*hexaèdres ou pyramides d'hexaèdres.*" (?!)

The greater intimacy of the combinations of antimony with fluorine than with chlorine is shown by the fact that the chlorantimoniates are decomposed by water, while the fluorine salts may be mixed with any quantity without suffering the least alteration, and reobtained on evaporation.

The behaviour of fluoantimoniate of fluoride of ammonium with reagents presents nothing remarkable. A saturated solution gives precipitates with the salts of lithium, barium, strontium, lime (even with $CaO\,CO^2$), alumina, peroxide of iron, protoxides of cobalt, nickel and manganese, oxides of lead, tin and mercury (crystalline with $HgONO^5$, gelatinous with HgCO). It gives no precipitates with salts of protoxides of iron or tin, oxides of zinc, cadmium, copper or uranium, morphine, quinine, cinchonine or strychnine. Chloride of platinum gives an immediate precipitate of platinochloride of ammonium (like the fluoantimoniate of potassium), the sodium salt gives no precipitate, nor is platinum reduced on boiling. All the fluoantimoniates, however, give precipitates with salts of suboxide of mercury and oxide of silver, and then a reduction of the metals, especially on applying heat. Chloride of gold is immediately reduced, the metal being separated in an extremely fine powder. On filtering and evaporating the solution, a sudden and violent disengagement of hydrofluoric acid takes place at a certain point of concentration. This remarkable reaction may perhaps be accounted for by supposing that the antimony combines with chlorine, and is contained in the solution at first as SbZ^5 (Z being fluorine and chlorine). But as this SbZ^5 cannot be very permanent, as follows from the known characters of $SbCl^5$ and the non-existence of SbF^5, a slight alteration of circumstances causes the evolution of so much Z that SbZ^5 is again reduced to SbZ^3. The great tendency of fluorine to assume the gaseous state would explain why this reduction should

* Ann. de Chim. et de Phys., lxvi. † Comptes Rendus, xx.

take place chiefly at the cost of the fluorine. This change may be thus represented:—

$$3(xRF+SbF^5)+2AuCl^3 \text{ give } 3\left(xRF+Sb\left\{\begin{matrix}F^5\\Cl^3\end{matrix}\right)\right)+2Au.$$

Consequently Z^5 would be $=(F^3+Cl^2)$. In any case this decomposition is deserving of further examination. It is evident that the decomposing character belongs less to the fluorine salt than to the fluoride of antimony present in it; and, in fact, pure fluoride of antimony reduces gold as perfectly as this salt. Chloride of antimony produces the same effect, as Levol* first showed. As there is no evolution of gas during the reduction of chloride of gold by fluoride of antimony, or at least none remarkable, the conjecture appears probable that a temporary compound, SbZ^5, is formed. However, SbF^5 cannot be obtained by this means, for on evaporating the liquid slowly, hydrofluoric acid is constantly disengaged, and the solution becomes turbid on adding water, showing the presence of chloride of antimony†.

Although the present investigation may not have brought our knowledge of the fluoantimoniates up to the desired degree of completion, still it has shown that they have the same general characters as the chlorantimoniates prepared by Jacquelain and Poggiale, and consequently the undeniable analogy of at least one series of chlorine salts with fluorine salts is proved. It may therefore be admissible to generalize the inference, and to recognise in this investigation a small contribution to a more consistent view of those salts which do not contain oxygen, inasmuch as it so closely connects the amphide salts of Berzelius (including the fluorine salts) with his double haloid salts, especially the chlorine salts, that any further distinction between them could no longer be regarded appropriate. The existence of differences between the chlorantimoniates and the fluoantimoniates does not at all impair the analogy; thus it appears that a hydrated fluoantimoniate of ammonia corresponding to the chlorine salt of Poggiale, cannot be obtained, and up to the present time no monobasic chlorantimoniates have been obtained‡.

The capability of the fluoantimonic acid to combine with 1, 2, or 3 equivs. of fluorine base is remarkable. A similar character was observed by Boullay and v. Bonsdorff in HgI and HgCl. This character of fluoride of antimony calls to mind the behaviour of antimonic acid; and the fact that the fluoride is more soluble than SbO^5 will sufficiently explain why it has a greater tendency than the latter to form well-defined characteristic compounds.

* N. Ann. de Chim. et de Phys., vol. lxxviii. Oxide of antimony, dissolved in a large quantity of hydrochloric acid, does not reduce chloride of gold; on the contrary, the reduction by means of SbF^3 is not hindered by the greatest excess of hydrofluoric acid.

† Evidently a decomposition of the fluoride of antimony by chlorine, but a secondary decomposition.

‡ I believe that I have succeeded in preparing AmCl+SbCl; but it is so extremely deliquescent, that it almost immediately disappears when pressed between bibulous paper.

It certainly would not contribute to a correct knowledge of these salts to assume the existence of several modifications of the fluoantimonic acid and its salts, as Fremy has done perhaps with less reason as regards antimonic acid.

Since the fluoride of antimony furnished such definite compounds with the alkaline fluorides, it seemed worth while to ascertain whether this was likewise the case with fluorides having the composition R^2F^3. Fluoride of aluminium being the most soluble of these bodies, was chosen for the purpose; solutions of Al^2F^3 and SbF^3, in proportions corresponding to the formula $Al^2F^3+3SbF^3$, when mixed and evaporated, gave a granular crust, which after being dried was no longer perfectly soluble in water. It contained 28·3 per cent. antimony and 16·3 per cent. aluminium, proportions at the best only approximatively represented by the very improbable formula $3Al^2F^3+SbF^3$, which requires 29·5 Sb and 19·2 Al. It must therefore remain undetermined for the present whether such compounds can be obtained.—Poggendorff's *Ann. der Physik und Chemie*, lxxxvii. 245.

On Essential Oil of Ginger. *By* A. Papousek.

The root of *Zingiber officinale* contains, according to Morin, an essential oil. To obtain this in sufficient quantity, ginger was submitted to distillation with water. With the water a yellow oil goes over, which possesses in a high degree the odour of ginger, and a burning aromatic taste. Its boiling-point is 475° F., its specific gravity 0·893.

The raw oil was deprived of water by pieces of fused chloride of calcium, and kept in a retort at a temperature below its boiling-point. At 302° F. a colourless oil evaporated, which on analysis gave the following numbers:—

Carbon	81·03	80	= 81·49
Hydrogen	11·58	69	11·72
Oxygen	7·39	5	6·79

$C^{80}H^{69}O^5=C^{80}H^{64}+5HO$. This oil is therefore a mixture of hydrates of a hydrocarbon isomerous with oil of turpentine.

As the oil acquired a darker colour, and began to undergo decomposition (as was known by the formation of water) when the heat was continued, the distillation was carried no further.

The raw oil was repeatedly distilled with anhydrous phosphoric acid. The yellow distillate gave the following numbers on analysis:—

Carbon	87·99	10	= 88·24
Hydrogen	11·88	8	11·76

The formula $C^{10}H^8$ places this oil with the numerous series of hydrocarbons usually characterized as the camphene series. The separation of the hydrate-water appears to be effected with equal ease by the action of muriatic acid, as by that of anhydrous phosphoric acid.

If muriatic acid gas be passed into the raw oil, the latter acquires a brown colour, even if care has been taken by cooling that the

action should not be too violent. The brown oil, saturated with muriatic acid, was washed with water, then submitted to distillation with water, and the product, which is of a yellowish colour and contains chlorine, dried over chloride of calcium. As shown by analysis, these operations, employed for the purpose of purification, partially decompose the muriatic acid compound, forming a mixture of a muriatic acid compound in an unchanged state with a hydrocarbon which has lost its muriatic acid. Analysis gave—

Carbon	73·39	80	73·45
Hydrogen	10·36	67	10·25
Chlorine		3	16·30

$C^{80}H^{67}Cl^{3}=C^{80}H^{64}+3ClH$. This formula may be split in the following manner:—$3(C^{20}H^{16},ClH)+C^{20}H^{16}$.

According to this, the essential oil of ginger belongs to the same class of essential oils as the coriander oil. The ginger employed so plentifully as an aromatic in cookery must therefore also belong to the camphene group of aromatics.—*Sitzungsb. der Akad. der Wissensch. zu Wien*, July 1852.

On Ledum palustre. *By* Fr. Rochleder *and* R. Schwartz.

Rochleder and Schwartz have extended the investigations of Willigk. They attempted to prepare the leditannic acid by the same process as the callutannic and rhodotannic acids*. For this purpose an alcoholic decoction of the leaves was distilled, the residue mixed with water, filtered to separate the precipitated green mass of wax, chlorophylle, fat and resin, treated with a solution of acetate of lead, the precipitate dissolved in dilute acetic acid, and the filtered liquid precipitated, at a boiling temperature, by tribasic acetate of lead, which gave a beautifully yellow precipitate, scarcely distinguishable from callutannate or rhodotannate of lead prepared in the same way. This precipitate, decomposed under water by sulphuretted hydrogen, the liquid heated to the boiling-point, and filtered hot, yielded a fine yellow solution of leditannic acid, which was evaporated to dryness in a retort filled with carbonic acid. The powdered residue, dried *in vacuo*, gave on analysis the following numbers, corresponding with the formula $C^{14}H^{9}O^{9}=C^{14}H^{6}O^{6}+3HO$:—

Carbon	50·89	14	= 84	50·91
Hydrogen	5·46	9	9	5·45
Oxygen	43·65	9	72	43·64

The aqueous solution of the acid, warmed and mixed with chloride of tin, gives a fine yellow precipitate, which when dried *in vacuo* has the following composition:—

Carbon	23·07	28	= 168	22·95
Hydrogen	3·05	21	21	2·87
Oxygen	23·88	21	168	22·95
Peroxide of tin	50·00	5	375	51·23

* Chem. Gaz., vol. x. p. 566.

An aqueous solution of leditannic acid, prepared in the above-described manner, yields, when acted upon by sulphuric acid, ledixanthine as a fine lemon-yellow or orange-red mass.

When an aqueous decoction of the leaves of *Ledum palustre* is evaporated until the residue has the consistence of honey, alcohol of 40° separates it into an insoluble and a soluble substance, the latter having a reddish-brown colour. The insoluble part is then only partially soluble in water. When the aqueous solution is heated to the boiling-point, a few drops of hydrochloric acid added, and then alcohol, a voluminous flocculent precipitate of a substance separates, which, when washed with alcohol and dried, gives a pale reddish powder. From the analysis of this body, it would appear to be a mixture of pectine and parapectine.

The alcoholic solution from the aqueous extract, when freed from alcohol and treated with solution of baryta, gave a yellow precipitate, which became rapidly brown, and consisted chiefly of leditannate of baryta. The filtered liquid was treated with carbonic acid, which separated baryta, together with a red product of the oxidation of the tannic acid retained in solution by the excess of baryta; the clear liquid was mixed with neutral acetate of lead, the precipitate still containing some tannic and citric acid was separated, when the filtrate, mixed with a slight excess of basic acetate of lead and alcohol, gave a white precipitate of a lead salt, which was washed with alcohol. Suspended in water and decomposed by sulphuretted hydrogen, it yielded a pale yellowish solution, which, on evaporation to dryness in an atmosphere of carbonic acid, left a residue, which, when heated with dilute sulphuric acid, immediately gave the smell of ericinole, while brown flocks were separated. This substance is ericoline; it is decomposed by acids into ericinole, and at least one other substance, which has the appearance of humus. Willigk observed an evolution of carbonic acid on distilling the extract containing ericoline with sulphuric acid. Ericoline, dried at 212° F., gave on analysis—

Carbon	34·42	16 =	96	34·41
Hydrogen	5·54	15	15	5·37
Oxygen	60·04	21	168	60·22

If the formula $C^{16} H^{15} O^{21}$ is a correct expression of the composition, this body might be broken up in the following manner:—

$$C^{16} H^{15} O^{21} = H^{6} O^{6} + C^{6} O^{12} + C^{10} H^{8} O^{2}.$$

Assuming that this formula should be doubled, the decomposition might be—

$$C^{32} H^{30} O^{42} = C^{12} H^{12} O^{12} + C^{10} H^{8} + C^{10} O^{20} + H^{8} O^{8}.$$

A further prosecution of this investigation promises to furnish some clue to the production of the oils $n(C^{5} H^{4})$, so numerous in the vegetable kingdom.—*Sitzungsbericht der Akad. der Wissenschaften zu Wien*, July 1852.

On Physaline. *By* V. Dessaignes *and* J. Chautard.

The bitter principle of *Physalis alkekengi* has been employed for some time with success in the treatment of fever, and the authors have consequently attempted its isolation. Every part of the Physalis is bitter, especially the leaves and fruit-capsules. The alcoholic extract of the plant yielded a bitter dark-coloured mass. The bitter principle is taken up by cold water, and was separated either by means of charcoal, from which it was afterwards dissolved by alcohol, or by shaking the aqueous solution with chloroform. The bitter principle thus obtained was pulverulent, slightly coloured, and very bitter.

Physaline, $C^{28}H^{32}O^{10}$, prepared in the last-mentioned manner, is when pure a white powder, with a faint tinge of yellow; its taste is at first faintly, afterwards permanently bitter; it is uncrystalline, softens at 356° or 374° F., then soon decomposes, burning with a smoky flame. It is very sparingly soluble in cold water, to which it communicates a bitter taste; more soluble in hot water, chloroform and alcohol; and sparingly soluble in æther and acids. It is also dissolved by ammonia, and remains unaltered after its volatilization. It is not precipitated by nitrate of silver and ammonia from the alcoholic solution; it is precipitated by an ammoniacal solution of acetate of lead. Dried *in vacuo*, it gave on analysis—

Carbon	63·78	63·57	28	63·64
Hydrogen	6·33	6·30	32	6·06
Oxygen	..	..	10	30·30

Compound of Physaline with Oxide of Lead, $C^{28}H^{30}O^{9}+3PbO$. —Prepared as above and dried *in vacuo*, it gave on analysis 54·34 per cent. oxide of lead; theory requires 56·70. The authors do not consider their analyses as decisive. The composition of cnicine, the bitter principle of *Carduus benedictus*, approximates very closely to the above:—Carbon, 62·9; hydrogen, 6·9; oxygen, 30·2. The fruit of the Physalis contains citric acid.—*Journ. de Pharm. et de Chim.*, 3rd ser., vol. xxi. p. 24–27.

Note on a new Alloy of Silver. *By* M. Germain Barruel.

In operating upon an argentiferous South American mineral, I obtained an ingot, which, judging from the mode of treatment and its dazzling whiteness, consisted evidently of very fine silver. Nevertheless, wishing to assay it, I experienced such a resistance under the shears, that I should have regarded it as containing 0·750 of silver; the assay however gave 0·994. Thus only 0·006 of other metals sufficed to give it this extraordinary power of resistance, without destroying its malleability.

M. de Cailleux, for whom I performed the experiment, had some knife-blades and a rasp of great hardness made from it, which he still possesses; he also requested me to follow out my investigations into the cause of this hardness existing in spite of so high a stan-

dard. Analysis gave me 0·0035 of iron, 0·002 of cobalt, and 0·0005 of nickel.

I have reproduced this alloy, varying the proportions in order to increase or diminish the degree of hardness. In one of the best, I employed equal parts of the three metals.

Not having met with any indication of such an alloy in the various treatises on chemistry, or in M. Berthier's learned 'Traité de la Voie Sèche,' and as it appears to be capable of various applications, I have thought it advisable to bring it before the public.—*Comptes Rendus*, Nov. 22, 1852, p. 759.

Upon Coriander Oil. By A. Kawalier.

The fruit of *Coriandrum sativum* was pounded and subjected to distillation with water. The oil which swims on the water which distils over is yellowish, nearly colourless, and possesses the odour and taste of coriander in a high degree. In a very diluted state the odour of this oil resembles that of orange-blossoms. Its specific gravity at 57° F. is 0·871, its boiling-point 302° F. In ascertaining the composition of this oil, for the first and second experiments it was allowed to stand over chloride of calcium; for the third, a large quantity of the oil was exposed in a retort on the oil-bath to a temperature below its boiling-point. The portion of oil which came over last was employed for the analysis. The air was removed from the distilling apparatus during the investigations by means of carbonic acid. The analysis gave—

Carbon....	77·62	78·01	77·73	10	= 750·0	77·92
Hydrogen	11·64	11·69	11·63	9	112·5	11·69
Oxygen ..	10·74	10·30	10·64	1	100·0	10·39

The formula $C^{10} H^9 O$ is the same that expresses the composition of Borneo camphor. Coriander oil is therefore to be considered as the hydrate of an oil having the same composition as oil of turpentine, $C^{10} H^9 O = C^{10} H^8 + HO$.

If the oil, mixed with anhydrous phosphoric acid, be repeatedly submitted to distillation, a yellowish oil, of a nauseous odour, of the composition of oil of turpentine, is obtained. This contains—

Carbon	88·28	10	= 750	88·23
Hydrogen.....	11·78	8	100	11·77

A stream of muriatic acid was passed into the crude oil, care being taken, by surrounding the vessel with ice, that the temperature should not rise too high. No crystalline compound was obtained in this manner. The product of the operation was washed with water to which some carbonate of soda had been added, dried over chloride of calcium, and submitted to analysis. It gave—

Carbon	67·51	67·51	40	= 3000·00	67·81
Hydrogen....	10·50	9·52	35	437·50	9·89
Chlorine	20·40	20·40	2	886·56	20·04
Oxygen.....	1·59	2·57	1	100·00	2·26

$C^{40} H^{35} Cl^2 O = (C^{20} H^{16}, HO + HCl) + (C^{20} H^{16}, ClH)$.

Another portion of powdered coriander, distilled with water, gave an oil agreeing in all its properties with the above-mentioned. It was deprived of water by chloride of calcium, and submitted to distillation by itself at a temperature below its boiling-point. The portion first evaporated possessed (as shown by analysis I.) the same composition as that which came over last (analysis II.):—

	I.	II.			
Carbon	85·67	85·47	80	= 6000·0	85·41
Hydrogen	11·58	11·59	66	825·0	11·74
Oxygen	2·75	2·94	2	200·0	2·85

$C^{80}H^{66}O^{2}=4(C^{20}H^{16})+2HO$, or $2(C^{20}H^{16})+2(C^{20}H^{16},HO)$.

Coriander oil, according to these experiments, is an oil of the camphene family, and contains various quantities of hydrate-water, which can be extracted by anhydrous phosphoric acid (not by chloride of calcium), in consequence of which it passes over into a hydrocarbon isomerous with oil of turpentine. The fruit of the coriander is frequently employed for the seasoning of cakes and similar articles. It follows, from the above results, that the coriander belongs to the spices of the camphene group, in which are included cloves, pepper, juniper, cummin, parsley, calamus, the rinds of citrons, oranges and limes, and wormwood.—*Sitzungsber. du Kaiserl. Akad. du Wiss.*, ix. p. 313.

ANALYTICAL CHEMISTRY.

On the Determination of Phosphoric Acid.

By Edward T. Bennett*.

The important influence which the soil exercises upon the development of the vegetable kingdom, in supplying a large portion of the materials which build up its organism, renders it desirable to possess an easy and certain method of estimating the more important inorganic constituents, as well of the soil as of the plants it produces. Phosphoric acid unquestionably plays an important part in organic life, and of late much labour and attention have been bestowed in improving the methods of estimating it.

M. A. Reynoso, in the Chemical Gazette, No. 217, has published a method, which, if it gave satisfactory results, certainly deserves to be preferred before all others that have been proposed. But since, from a theoretical point of view, well-grounded doubts of its success can be raised, it seemed worth while to institute a few experiments as to its practicability. The method is founded upon the insolubility of phosphate of deutoxide of tin in nitric acid. A

* Communicated by the Author.

weighed quantity of tin, yielding a known amount of stannic acid, along with the substance to be investigated, is boiled with an excess of nitric acid till complete oxidation has taken place. The produced precipitate of mixed phosphate of deutoxide of tin and stannic acid is filtered, washed, and its quantity ascertained. The excess in weight above what the tin alone would have given, is taken as the quantity of phosphoric acid in the substance investigated. We must recollect, that, for a comparatively small quantity of phosphoric acid, a large amount of tin is requisite to ensure complete precipitation. In the mechanical treatment, for example in the washing of a large precipitate, small errors of a few millegrammes are very liable to occur, all of which naturally fall upon the phosphoric acid. Further, it is not improbable that in a very compound substance other bodies besides phosphoric acid may be precipitated; and again, it is a question, even when a large amount of tin is employed, whether small quantities of the phosphoric acid are not liable to remain in the solution. From the experiments which M. Reynoso adduces in confirmation of his method, it is clear that in some instances this was the case.

In order to ascertain whether, in the presence of other constituents of soils and ashes, anything besides phosphoric acid was precipitated by boiling with nitric acid, some tin was taken, mixed with an equal or somewhat smaller quantity of iron, and boiled for perhaps an hour with strong nitric acid diluted with its bulk of water; a yellowish-white crystalline powder was obtained, which on washing on a filter passed through turbid, and appeared almost completely to dissolve in an excess of water. On continued boiling of this aqueous solution, the tin is reprecipitated. This experiment, which was many times repeated with different proportions of the substances employed, gives the interesting result, that tin, which when boiled by itself with nitric acid is so readily converted into insoluble deutoxide, produces, in the presence of iron and nitric acid, soluble double compounds, probably consisting of the oxides of iron and tin combined with nitric acid.

If combinations of phosphoric acid are dissolved in the smallest possible quantity of nitric acid, and to such a solution neutral chloride of tin and an excess of sulphate of soda are added, all the tin is precipitated as deutoxide, together with the whole quantity of phosphoric acid. If the bases are lime or alumina, they remain in solution. In this way it seemed not improbable that phosphoric acid might be determined in a satisfactory manner. With this view a series of experiments were made, which have shown, that when, besides alumina and lime, iron also is present, a large proportion of it is precipitated along with the tin and phosphoric acid, and in a form insoluble in water. A favourable result has in vain been sought for by various changes in the process and manipulation.

We can therefore safely conclude, that to substances containing iron M. Reynoso's method is inapplicable; and even where it is absent, many precautions and the greatest care must be taken to

avoid the numerous errors to which this method, under any circumstances, seems liable, and to obtain a certain and accurate result.

Queenwood, Dec. 10, 1852.

PATENTS.

Patent granted to John Brazil, *for the Preparation of Dye-woods.*

The first part of this invention consists in the employment of soap or saponaceous compounds in water to liberate the colouring matter of madder, garancine, or other "dye-stuffs," in the process of dyeing. The proportions which have been found to answer are as follows:—$\frac{1}{2}$ a lb. of soap (by preference, palm-oil soap) is employed for every 10 lbs. of madder, and to the mixture is added the usual quantity of chalk; or, for the sake of œconomy, the patentee uses about half or two-thirds of the soap-liquor from the beck or vat in which the pieces of goods or fabrics have been soaped the first time, instead of the first-mentioned soap. In either case, the madder is added to the soap-liquor before introducing the fabrics into the dye-vats; and it is preferred to introduce them into the dye-bath when the latter is at the temperature of about 70° or 80° F., and to raise it to 180° in about an hour and a quarter.

This invention consists, secondly, in using borax, either separately or in conjunction with soap or other saponaceous compounds, in water, in order to liberate the colouring matter of madder, garancine, or other dye-stuffs, in the act of dyeing. The following are suitable proportions:—12 lbs of madder, $\frac{1}{2}$ a lb. of soap, and $\frac{1}{4}$ of a lb. of borax, with the usual quantity of ground chalk, to be used as above described.

The third part of this invention consists in saturating the fabrics to be dyed or printed with a soapy or saponaceous solution, which must be dried in the goods previous to a mordant being applied. The solution is prepared by adding 1 lb. of soap to 12 gallons of water, and is used either hot or cold; this is the strength at which the solution is to be employed when the piece of goods is conducted into the solution in a dry state; but when it is introduced wet from the bleaching process, the solution must be a little stronger. The patentee has found the following solution to answer very well, although he does not consider it quite equal to the preceding one:—He takes the soap-liquor, in which the pieces of goods have been soaped, from the soap-liquor beck, and adds as much resin as it will dissolve; and then he passes the fabric through it, as before mentioned; when the fabric has been dried, it will be ready for the usual mordants. He has also used with advantage a solution made by dissolving 1 lb. of borax in 6 gallons of water, and then adding as much resin as it will dissolve.

The last part of the invention consists in facilitating the extraction of the colouring matter from dye-woods, or other dye-stuffs, by the employment of a solution of soap, or a solution of borax, or a

solution of both combined, of such strength as the nature of the dye-woods or dye-stuffs may require.—Sealed June 24, 1851.

Patent granted to P. Claussen, *for Improvements in Saline and Metallic Compounds.*

The first part of this invention relates to the manufacture of certain saline compounds, such as nitrate of potash, and consists in treating ammonia, and certain ammoniacal compounds evolving ammonia, in such manner that the volatile alkali may suffer decomposition and oxidation, so that certain nitracids, and especially nitric acid, may be formed,—lime, potash, soda, or other suitable base, being presented to the nascent nitracid, in order that nitrate of lime, potash, or soda may be produced. To assist the oxidation of the ammonia, the patentee employs an apparatus containing pumice-stone, charcoal, coke, platinum foil, spongy platinum, or other substances which present an extended surface, possessing the property of absorbing large quantities of oxygen. The ammoniacal liquid is allowed to pass over the surface of the spongy platinum or other substance; and it is then, in its oxidated state, brought into contact with a suitable base, so as to form a nitrate of the same. The patentee states, that when using an ammoniacal salt (such as the sulphate of ammonia), he first presents to the salt some suitable body (such as lime) with which the acid will combine, setting the ammonia free; the part of the apparatus in which this change takes place must be closed, to prevent the escape of the liberated ammonia into the air. The ammonia, being absorbed by water, is allowed to drop on to the surface of the spongy platinum or other oxidating substance, and then into a solution of the base of the future nitrate. The above process may be employed in the nitrification of the ammonia obtained in the manufacture of gas from coal.

The second part of the invention relates to the manufacture of soda salts, and consists in the conversion of sulphate of soda, whether made directly or produced as a residuum, into caustic soda (hydrate of soda) and carbonate of soda. Thus to a solution of sulphate of soda is added a suitable proportion of some substance, which having a greater affinity for sulphuric acid than soda will decompose that salt and set the soda free. If, for example, the hydrate of lime, baryta, or strontia be used, sulphate of lime, baryta, or strontia will be formed, and hydrate of soda be left in solution. By long exposure to the atmosphere, carbonic acid will be absorbed, and the hydrate of soda will thereby be converted into carbonate of soda. The decomposition of the sulphate of soda is facilitated by the application of heat.

It is also proposed by the patentee to manufacture hydrate of soda and carbonate of soda direct from common salt, by decomposing that substance by certain organic acids (which are afterwards decomposed by heat); or by gaseous acids; or by hydrates, oxides, peroxides, and certain metallic bases; or by certain carbonates, carbonate of ammonia excepted.—Sealed Feb. 3, 1852.

THE CHEMICAL GAZETTE.

No. CCXLVI.—January 15, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Resin of Jalap. *By* W. MAYER.

THE rhizomes of *Convolvulus Schiedeanus*, Zucc., known as jalap-roots, contain an active principle, a resin which has been repeatedly made the subject of chemical investigation by Cadet de Gassicourt, Tromsdorff, Gobel, Buchner, Herberger, Kayser and Sandrock. Johnston examined the resin from the rhizome of *Convolvulus orizabensis*, Pell. Buchner and Herberger believed they had detected a basic substance, jalapine, and a resinous acid. Kayser* extracted the resin with æther, and found that the insoluble residue had the complicated formula $C^{42}H^{35}O^{20}$, was identical with jalapine, and by treatment with bases was converted into an acid soluble in water, composed of $C^{42}H^{35}O^{20}+HO$. He found, moreover, that both this acid, which he called *hydrorhodeoretine*, and the original resin, rhodeoretine, were broken up, by treatment with hydrochloric acid, into sugar and a neutral substance unacted upon by either concentrated potash or concentrated sulphuric acid. He called this body *rhodeoretinole*. Sandrock obtained results essentially different from those of Kayser. He considered the part insoluble in æther to consist of two resins, one of which was precipitated by acetate of lead from the alcoholic solution, the other not. He described both resins as being converted by boiling with alkalies into soluble acids, of which one, ipomic acid, was precipitated by basic acetate of lead from the neutral potash salt; the other, jalapic acid, not.

The resin extracted from the rhizomes of *C. Schiedeanus* by alcohol, and partly decolorized by treatment with water and animal charcoal, is but partly soluble in æther; and it is the insoluble part which Mayer has examined.

Rhodeoretine.—The rhizomes were treated with boiling water until no more colouring matter was extracted. They were then dried, coarsely powdered, and digested three times with twice their weight of alcohol (0·833 sp. gr.). The alcoholic extract was mixed with water until it began to become turbid, and treated twice with bone-charcoal. The alcohol was then distilled off from the pale yellowish filtrate; a yellow brittle resin remained, which was powdered, digested with æther four or five times, dissolved three times in the least possible quantity of absolute alcohol, and precipitated by æther in order to effect the perfect separation of a minute quantity of the

* Chem. Gaz., vol. iii. p. 15.

resin soluble in æther. Owing to the neglect of this purification, Kayser estimated the per-centage of carbon nearly 1·5 per cent. too high. Thus prepared, and dried at 212° F., rhodeoretine resembles in appearance the finest gum-arabic; it is odourless, tasteless, brittle, colourless, and transparent in thin pieces, perfectly white when powdered. When it contains but a small amount of water, it becomes soft below 212° F., and may be drawn out into fine threads having a pearly lustre. It softens at 265°·8 F., melts at 302° F. to a yellowish liquid; above 311° F. it begins to decompose. Its alcoholic solution has a feeble acid reaction. It appears to be the active principle of jalap*; 3 or 4 grs. caused repeated and violent purging. It burns with difficulty, and its analysis could only be effected by means of a mixture of 9 parts of chromate of lead and 1 part bichromate of potash, the front part of the tube being charged with chromate of lead alone. Analysis gave—

Carbon	55·01	54·56	54·53	54·57	72	54·75
Hydrogen	7·89	8·07	7·89	7·89	60	7·73
Oxygen	37·10	37·37	37·58	37·54	37	37·52

On the analysis of rhodeoretine, which had not been precipitated by æther, 56·76 carbon and 8·16 hydrogen were obtained. Kayser obtained—

Carbon	56·06	55·87	42	56·37
Hydrogen	7·94	7·89	35	7·84
Oxygen	36·00	36·24	20	35·79

The resin, melted at 302° F., lost 1 equiv. of water, and gave—

Carbon	54·86	55·21	72	55·38
Hydrogen	8·04	8·00	60	7·69
Oxygen	37·10	36·79	36	36·93

Mayer states that he would not have ventured to assign to this body so high an atomic weight except on account of the combinations of the modification soluble in water and its products of decomposition.

Rhodeoretine is but slightly soluble in water, very soluble in alcohol, insoluble in æther. The alcoholic solution is precipitated both by water and alcohol. It is soluble in potash, soda, ammonia and baryta water, more quickly when warm. Acids do not again precipitate it from these solutions; it has become soluble in water. It is little soluble in cold solutions of carbonate of soda or potash, more so when boiled. It dissolves readily in acetic acid, very slowly in cold dilute nitric acid, more quickly and with decomposition when heat is applied; concentrated nitric acid acts upon it energetically, with considerable evolution of nitrous oxide and elevation of temperature. Concentrated sulphuric acid dissolves the resin, and communicates a beautiful red colour, which changes to brown in a few hours. If the solution is diluted with water while red, a brownish oleaginous body, of agreeable odour resembling fresh plums, sepa-

* Schlossberger is not of this opinion. See his Organ. Chemie, 2nd edition, . 280.

rates, and the liquid contains sugar. Heated on platinum foil, the resin melts, turns brown, and burns with a bright smoky flame, disengaging a peculiar empyreumatic odour, resembling caramel. A coal remains.

Rhodeoretinic Acid.—This is the body formed by the action of strong bases upon the above resin. The change consists in the assimilation of 3 equivs. of water. It was prepared by introducing 100 grms. of pure rhodeoretine into 1 lb. of baryta-water, and stirring the mixture while heating till it boiled. The resin dissolved quickly and entirely. The baryta was separated from the cold solution by sulphuric acid in very slight excess, which was removed by means of carbonate of lead. The colourless filtrate, evaporated to dryness in a water-bath, left a substance exactly resembling rhodeoretine, except that it is very hygroscopic. Above 212° F. it softens, and melts between 212° and 248° F. Above 248° F. decomposition commences. It has no smell; the aqueous solution has a smell very like quinces and a strong acid reaction. It and its salts were all burnt in the same manner as the rhodeoretine:—

Carbon	52·44	52·61	52·48	52·89	72	52·94
Hydrogen	7·93	8·04	7·87	7·82	64	7·84
Oxygen	39·63	39·35	39·65	39·29	40	39·22

Rhodeoretinic acid is insoluble in æther, soluble in all proportions in alcohol and water. The aqueous solutions of the acid or the neutral ammonia salt are not precipitated by any neutral metallic salt; basic acetate of lead gives a very voluminous, flocculent, white precipitate. The acid expels carbonic acid from alkaline and earthy carbonates, as well as from carbonate of lead, especially by boiling. It behaves towards acetic, nitric, and concentrated sulphuric acid precisely as rhodeoretine does.

Rhodeoretinate of Potash, $C^{72}H^{62}O^{38}$, KO, HO.—Rhodeoretine is only partially converted into the soluble acid modification by boiling with a solution of carbonate of potash. This is why Kayser found too little potash in his salt. Mayer prepared it by neutralizing a solution of the acid with carbonate of potash, evaporating to dryness, and dissolving the residue in alcohol. The salt is slightly yellow, amorphous, melts between 212° and 230° F.; soluble in water, sparingly in alcohol; its solution has a bitter taste and a smell of quinces. Analysis gave—

Carbon	..	..	50·48	72	50·57
Hydrogen	..	..	7·55	63	7·37
Potash	5·66	5·65	..	1	5·52
Oxygen	..	..	..	39	36·54

Rhodeoretinate of Baryta, $C^{72}H^{62}O^{38}$, BaO, HO.—Caustic baryta gives with excess of rhodeoretine an acid salt; when, on the contrary, baryta is in excess, a neutral salt is formed. The former was prepared by boiling an excess of rhodeoretine with baryta-water, filtering, adding baryta-water until the solution was feebly alkaline, and then passing carbonic acid through it until neutralized, again warming, filtering, and evaporating to dryness in a water-bath. It

is an amorphous, yellowish, brittle, translucent mass, with a bitter taste and a smell of quince. It melts between 212° and 230°, is readily soluble in water and alcohol, and behaves like the potash salt when heated. Analysis gave—

				Kayser.			
Carbon			48·85	50·68	50·61	72	48·89
Hydrogen			7·25	7·55	7·54	63	7·12
Baryta.....	8·83	8·64	..	7·63	7·63	1	8·65
Oxygen			..	..	..	39	35·34

Neutral Baryta Salt, $C^{72}H^{62}O^{38}$, 2BaO.—Formed when rhodeoretine is treated with excess of baryta-water at the ordinary temperature, but more rapidly on boiling. Carbonic acid is passed through the boiling alkaline solution, and the neutral filtrate evaporated to dryness. Except in composition, and a less distinct smell of its solution, it resembles the acid salt in its characters. Analysis gave 16·14 and 16·04 BaO; theory requires 16·08.

Rhodeoretinate of Lime, $C^{72}H^{62}O^{38}$ 2CaO.—Prepared in a manner similar to the last salt. Amorphous, gum-like, yellowish mass, readily soluble in water and alcohol. Dried at 212°, analysis gave 6·17 and 6·20 per cent. CaO; theory requires 6·55.

Products of the Action of Sulphuric Acid upon Rhodeoretine.—Kayser showed that rhodeoretine dissolved in alcohol was broken up into an oily body, rhodeoretinole, and sugar by the long-continued action of hydrochloric acid. Mayer succeeded in effecting the same decomposition by boiling the aqueous solution of rhodeoretinic acid with very dilute mineral acids, and obtained a purer product by this method. To a boiling solution of 30 grms. of the acid in 300 grms. of water he added a mixture of 20 grms. sulphuric acid and 200 water. The decomposition commenced almost immediately, the liquid became milky, and a yellowish oil* sunk to the bottom. The complete decomposition requires long boiling when the above proportions are used. The acid liquid retains a minute quantity of the oily body in solution, which separates on gradual cooling in delicate white acicular crystals. Mayer states that this substance presents distinctly acid characters, and proposes to give it the name *rhodeoretinolic acid.* It solidified at 59° F., in the liquid from which it had separated, after about twelve hours, to a soft fatty mass, was then separated by a moistened filter, and repeatedly washed with boiling water to separate all the sulphuric acid.

Rhodeoretinolic acid is very sparingly soluble in pure water, rather more soluble in acidulated water, very soluble in alcohol, less so in æther. It crystallizes from the aqueous solution, on gradual cooling, in colourless, acicular, microscopic needles. It cannot be crystallized from alcohol or æther. At 77° F. it softens, and melts between 104° and 113° F. to a yellowish liquid, solidifying when cooled to an indistinct crystalline mass, slightly coloured, and resembling

* Kayser says that his rhodeoretinole was a "dark brown-yellow oily liquid," which was evidently owing to his having used too concentrated acid in its preparation.

many fatty acids in appearance. It softens and feels fatty between the fingers, gives a greasy spot on paper, has an acid reaction, and an acrid bitter taste; it is odourless, but when melted in water diffuses a peculiar odour, very much like that of *siliqua dulcis*. Dried at 212°, and then over sulphuric acid in a vacuum, it gave on analysis—

			Kayser.		
Carbon	65·56	65·38	66·38	36	65·45
Hydrogen	10·70	10·72	10·67	34	10·30
Oxygen	23·74	23·90	22·95	10	24·25

It forms salts with bases. The alkaline salts are very soluble in water, the earthy salts less so; the salts of lead, silver and copper, insoluble in water, very sparingly soluble in alcohol. The acid expels carbonic acid from the alkaline and earthy carbonates. Heated upon platinum foil, it melts, volatilizes *apparently* without decomposition, burns with a bright flame, leaving a small quantity of coal and giving off a very acrid odour resembling sebacic acid. With concentrated sulphuric acid it gives a yellow, and then red colour, like rhodeoretine and rhodeoretinic acid. The production of this colour indicates the formation of rhodeoretinolic acid.

Rhodeoretinolate of Baryta, $C^{36}H^{33}O^{9}BaO$.—Prepared by mixing an alcoholic solution of the acid with a slight excess of baryta-water, passing carbonic acid through the liquid, and filtering while hot. The crystals formed on cooling were colourless and acicular. Dried at 212°, the salt gave on analysis 19·55 per cent. BaO; theory requires 19·24. It is sparingly soluble in cold water, more readily in warm water or in alcohol.

Rhodeoretinolate of Silver.—Prepared by precipitating the neutral ammonia salt with nitrate of silver. It appears to decompose very readily under the influence of light, to which circumstance is owing the excess of silver in the analysis, which gave 25·61 and 26·00 per cent., while the formula $C^{36}H^{33}O^{9}$, AgO requires 24·71.

Rhodeoretinolate of Lead.—Acetate of lead gives a voluminous white precipitate with rhodeoretinolate of ammonia, which becomes a horny yellowish mass when dried *in vacuo*. Analysis gave 33·89 and 33·82 per cent. PbO; theory requires for the formula $2(C^{36}H^{33}O^{9})+3PbO$, 33·54 per cent.

Rhodeoretinolate of Copper, $2(C^{36}H^{33}O^{9})+3CuO$.—Bluish-green; melts at 230° F. to a clear liquid, solidifying to an amorphous mass of dark green colour and great brilliancy. Dried at 248° F., analysis gave 15·53 and 15·62 per cent. CuO; theory requires 15·74.

Examination of the Acid Liquid left after separating the Rhodeoretinolic Acid obtained by the Decomposition of Rhodeoretine.—The sulphuric acid was removed by means of carbonate of lead, the dissolved oxide of lead separated by sulphuretted hydrogen, and the clear liquid evaporated to about one-tenth. A small quantity of rhodeoretinolic acid separated on cooling; this was removed by repeated agitation with æther, and on evaporating to dryness in a water-bath, a brownish syrupy mass remained, presenting all the characters of sugar. It dissolved readily in water, sparingly in

absolute alcohol, was sweet and without odour. Heated with potash and sulphate of copper, it reduced the metal; with purified bile and sulphuric acid, it gave a purple colour; and with yeast, it fermented. Mayer could not obtain it in crystals, or prepare the characteristic compound of sugar and chloride of sodium. He therefore prepared the baryta compound by mixing alcoholic solutions of hydrate of baryta and sugar. The precipitate, dried *in vacuo*, was almost white, readily soluble in water, and gave on analysis—

Carbon	28·74	28·92	12	29·09
Hydrogen	4·63	4·79	11	4·44
Baryta	31·05	..	1	30·91
Oxygen	35·58	..	11	35·56

These numbers resemble those obtained by E. Peligot, W. Stein and E. Soubeiran, for the baryta compound of cane-sugar. Peligot found 31·31, 30·90, and 30·80 per cent. baryta; Stein, 31·03; Soubeiran, 30·90, 31·10 and 30·80. Soubeiran gives as the formula of the compound of grape-sugar with baryta, $C^{24}H^{24}O^{24}+3BaO$, while Peligot gives $C^{24}H^{24}O^{24}+3BaO+4HO$. Mayer therefore prepared the grape-sugar compound with baryta, and found it gave on analysis 31·04 per cent. of BaO, agreeing with the formula $C^{12}H^{11}O^{11}+BaO$. The body analysed suffered no further loss of weight after having been kept for eight days *in vacuo* over sulphuric acid.

The action of hydrochloric acid or emulsine upon rhodeoretinic acid was precisely the same as the action of sulphuric acid.

Action of Nitric Acid upon Rhodeoretinic Acid and Rhodeoretinolic Acid.—The products of this action are oxalic acid and a white, crystalline, non-nitrogenous acid, identical or isomeric with sebacic acid. The formation of sebacic acid has hitherto been regarded as a decisive indication of the presence of oleic acid. Mayer proposes that the acid should be called *ipomic acid* until its relation to sebacic acid has been ascertained. He obtained it in the following manner:—Rhodeoretinic acid was treated with nitric acid (1·30 sp. gr.); after a few minutes a brisk action commenced even in the cold; the temperature rose, and nitrous vapours were evolved. When heat is applied in the first instance, the action is too violent. When the first reaction was over, the mixture was warmed for six or eight hours in a covered vessel in a water-bath, at the end of which time scarcely any nitrous acid was disengaged. It was then poured into a basin, and the nitric acid driven off, water being constantly added. A pale yellow liquid then remained, which became almost solid on cooling. This mass was then mixed with a little water, and washed upon a filter with cold water; ipomic acid remained as a white flocculent body, and the filtrate gave oxalic acid on evaporation, together with a yellow amorphous substance, which appeared to be an intermediate product. The same reaction takes place, but with greater violence, when fuming nitric acid is employed. If, on the contrary, rhodeoretinic acid is digested for twelve hours with weak nitric acid (1·16 to 1·18 sp. gr.) in the cold, the liquid contains unaltered rhodeoretinolic acid and sugar, which respectively yield ipomic and oxalic acids by

the further action of nitric acid. Mayer then treated rhodeoretinolic acid with nitric acid, and obtained ipomic and oxalic acids, showing that in the former reaction the oxalic acid was not solely formed from the sugar resulting from the first stage of the decomposition of rhodeoretinic acid.

Ipomic Acid.—The impure product was washed with water, then treated again for six hours with nitric acid, which was driven off by heat, and the ipomic acid twice crystallized from boiling water. It was then brilliantly white, without smell, had an acid reaction and taste, irritating the throat. It consisted of microscopic acicular crystals, but was sometimes obtained in very thin flexible laminæ, without any obvious difference in the circumstances of its crystallization. It sublimed between watch-glasses, forming stellar groups of needles, and leaving a slight carbonaceous residue. Sebacic acid, sublimed in the same manner, gave larger and more distinct crystals. The vapour is irritating to the throat, and smells like those of fatty acids. The acid melts to a colourless oil, lighter than water, and solidifies on cooling in crystals similar to those obtained by sublimation. Its melting-point is 219°·2 F., while that of sebacic acid was found by Henneberg to be 260°·6 F. Three times recrystallized and dried at 212° F., it gave on analysis—

					Sebacic acid.		
Carbon	59·27	59·67	59·38	10 59·40	59·41	*59·63	*59·20†
Hydrogen	8·94	9·10	8·98	9 8·91	9·19	8·98	8·90
Oxygen	31·79	31·23	31·64	4 31·69	31·40	31·39	31·90

According to these analyses, ipomic acid has the formula $C^{10}H^{9}O^{4}$, and appears to be homologous with pimelic acid, $C^{7}H^{6}O^{4}$, and suberic acid, $C^{8}H^{7}O^{4}$, which bodies it likewise resembles in its formation. Ipomic acid is not altered by digestion with strong nitric acid for eight days in a water-bath; but this must not be considered as a proof that it would not be altered by long-continued action; for, as Schlieper‡ has shown, sebacic acid is converted by similar means into 2 equivs. of pyrotartaric acid :—

$$C^{10}H^{9}O^{4}+5O=2(C^{5}H^{4}O^{4})+HO, \text{ or}$$
$$C^{20}H^{18}O^{8}+10O=(C^{10}H^{8}O^{8})+2HO.$$

Ipomic acid is but sparingly soluble in cold water, very readily in boiling water, alcohol or æther. It forms salts, with the exception of the alkaline ipomates, generally of slight solubility.

Ipomate of Ammonia, $C^{10}H^{8}O^{3}+AmO+C^{10}H^{8}O^{3}+HO$.—When ipomic acid is dissolved in ammonia and the solution evaporated in a water-bath, ammonia is continually separated, and an acid salt is obtained having probably the above formula, similar to that established by Berzelius for the sebate of ammonia. This behaviour of the ammonia salt renders the preparation of the other salts difficult, and may perhaps account for the deficiency of nearly 1 per cent. of oxide of silver in the analysis of the silver salt.

Ipomate of Silver, $C^{10}H^{8}O^{3}+AgO$.—Prepared by precipitation,

* Dumas and Peligot. † Redtenbacher. ‡ Chem. Gaz., vii. p. 229.

white, insoluble in water, sparingly soluble in alcohol and æther; heated in a test-tube, it gives a sublimate undistinguishable from sublimed ipomic acid. Analysis gave 54·77 and 55·00 per cent. AgO, while theory requires 55·76.

Ipomate of Copper, $C^{10}H^{8}O^{3}+CuO$.—Salts of copper give a bluish-green precipitate with ipomate of ammonia, very sparingly soluble in water. Analysis gave 29·97 per cent. CuO; theory requires 30·30 per cent.

Ipomate of Lead, $C^{10}H^{8}O^{3}+PbO$.—White powder, insoluble in water. Analysis gave 54·70 per cent. PbO; theory requires 54·00.

Ipomate of ammonia gives a precipitate with chloride of calcium, which only after some considerable time becomes crystalline; sebate of ammonia gives a crystalline precipitate at once. Perchloride of iron gives a flesh-red, and bichloride of platinum a yellow precipitate, soluble in boiling water; it separates on cooling, and becomes crystalline after some time.

Mayer infers from the above experiments that rhodeoretine has the composition $C^{72}H^{60}O^{36}+Aq$; that on melting it loses an equivalent of water, without further alteration; boiled with solutions of strong bases, it is converted into a soluble acid body, differing from it in composition only by containing 3 equivs. more water than the hydrated, or 4 equivs. more than the anhydrous rhodeoretine. The rhodeoretinic acid is bibasic, its composition being expressed by the formula $C^{72}H^{62}O^{38}+2HO$; it forms salts with 1 or 2 equivs. of base. Under the influence of mineral acids or emulsine, it is decomposed with production of rhodeoretinolic acid and sugar, $C^{72}H^{64}O^{40}+6HO=C^{36}H^{34}O^{10}+3(C^{12}H^{12}O^{12})$. A quantitative determination of the rhodeoretinolic acid thus formed gave 38·20 per cent.; theory requires 38·71. The difference of 0·51 per cent. may safely be regarded as owing to an error of observation. Nitric acid, after effecting the above decomposition, decomposes the products by its further action, the rhodeoretinolic acid into ipomic and oxalic acids, the sugar into oxalic acid:—

$$C^{72}H^{64}O^{40}+24NO^{5}=3(C^{10}H^{9}O^{4})+21(C^{2}HO^{4})+16HO+24NO^{3},$$

or

$$C^{36}H^{34}O^{10}+6NO^{5}=3(C^{10}H^{9}O^{4})+3(C^{2}HO^{4})+4HO+6NO^{2}.$$

He likewise infers that rhodeoretinolic acid and grape-sugar minus water pre-exist in rhodeoretinic acid, in other words, that it is a conjugate compound of sugar, similar in constitution to the following:—

Salicine:—

$$C^{26}H^{18}O^{14}+2HO=\underbrace{C^{12}H^{12}O^{12}}_{\text{Sugar.}}+\underbrace{C^{14}H^{8}O^{4}}_{\text{Saligenine.}}$$

Phloridzine:—

$$C^{42}H^{24}O^{20}+2HO=C^{12}H^{12}O^{12}+\underbrace{C^{30}H^{14}O^{10}}_{\text{Phloretine.}}$$

Populine:—

$$C^{40}H^{22}O^{16}+4HO=C^{12}H^{12}O^{12}+\underbrace{C^{14}H^{6}O^{4}}_{\text{Benzoic acid.}}+\underbrace{C^{14}H^{8}O^{4}}_{\text{Saligenine.}}$$

Tannic acid:—

$$C^{40}H^{18}O^{26}+10HO=C^{12}H^{12}O^{12}+2(\underbrace{C^{14}H^{8}O^{12}}_{\text{Gallic acid.}}).$$

Rhodeoretinic acid:—

$$C^{72}H^{64}O^{40}+6HO=3(C^{12}H^{12}O^{12})+\underbrace{C^{36}H^{34}O^{10}}_{\text{Rhodeoretinolic acid.}}$$

With regard to Kayser's results, Mayer observes that the formulæ which he assigned to rhodeoretine and rhodeoretinic acid are incorrect; that he determined their per-centage of carbon too high, because he analysed impure bodies; that his analysis of rhodeoretinate of potash was incorrect, because he did not pay attention to the behaviour of the acid to carbonate of potash; that he proposed an erroneous theory of the decomposition of rhodeoretinic acid into sugar and rhodeoretinolic acid, which induced him to regard his nearly-correct analysis of rhodeoretinole as incorrect, but that he was perfectly right in considering that part of jalap-resin insoluble in æther to be a complex body.

With regard to the views of Sandrock, he is of opinion that they are founded upon a misinterpretation of the observed facts. The reasons given by Sandrock for his opinion, that the part of jalap-resin insoluble in æther consists of two resins, he regards as insufficient, inasmuch as they only prove that the lead salt of the resinous acid is not very sparingly soluble in water, a fact already mentioned by Kayser. Mayer likewise remarks, that his analyses show that the resinous acid obtained from the lead precipitate by means of sulphuretted hydrogen has the same composition as that obtained by decomposing the baryta salt by sulphuric acid, although Sandrock called the former ipomic acid, the latter a mixture of ipomic and jalapic acids. The jalapine of Buchner and Herberger is identical with the rhodeoretine of Kayser and Mayer and the β-resin of Sandrock.—*Ann. der Chem. und Pharm.*, lxxxiii. p. 121.

On some new Compounds of Iridium. *By* M. Skoblikoff.

The author has prepared the representatives, in the series of salts of iridium, of the green platinum salt of Magnus and of Gros' platinum base, and also some new compounds of iridium.

Protochloride of iridium was first prepared by heat from the perchloride. The resinous brown substance remaining after heating the perchloride was dissolved in carbonate of ammonia. The solution was supersaturated with muriatic acid, when a granular yellow precipitate was deposited, which is insoluble both in cold and hot water. It is the

Ammoniacal Protochloride of Iridium, $IrClNH^3$, and corresponds to the green platinum salt of Magnus. From this it is distinguished by the form of the crystals and by its colour. Heated on platinum, it is decomposed into muriate of ammonia, muriatic acid and iridium. This salt may be regarded as chloride of ammonium, in which 1 equiv. of hydrogen is displaced by 1 equiv. of iridium. Analysis:—

Iridium	64·79	65·24	1 =	1233·20	65·28
Chlorine	23·33	23·43	1	443·20	23·45
Ammonia	10·58	11·26	1	212·50	11·27

The Iridium Base, $IrCl N^2 H^6 O$, which corresponds with the platinum base of Gros, is obtained in combination with nitric acid by heating the preceding yellow salt of iridium with that acid; it

becomes brown rapidly, and changes into a yellow, granular, crystalline mass, which dissolves readily in water. Very little more nitric acid than is just necessary must be added, too large a quantity producing a mass which does not crystallize.

The Nitrate of the Iridium Base, $IrCl\,N^2\,H^6\,O, NO^5$, is obtained by recrystallization from its watery solution in shining, yellow, laminar crystals. If the salt is mixed with copper filings, and sulphuric acid poured over it, the presence of nitric acid may be readily recognised by the red vapours which rise. The nitric acid can be displaced by other acids; the salts formed evolve ammonia when heated to redness with alkalies. Chlorine may also always be shown to exist in them.

Sulphuretted hydrogen throws down only a small quantity of sulphuret of iridium. The author considers this substance as a compound of nitric acid with an iridium base which contains chlorine, nitrogen and hydrogen combined in such a manner that their usual reactions are no longer observable. Analysis gave:—

Iridium	42·85	42·85	1 =	1233·20	42·87
Chlorine	15·41	15·41	1	443·20	15·42
Hydrogen	..	..	6	75·00	2·61
Nitrogen	..	2·75	3	525·00	18·25
Oxygen	..	..	6	600·00	20·85

Sulphate of the Iridium Base, $IrCl\,N^2\,H^6\,O, SO^3$, is obtained by treating the nitric salt above described with dilute sulphuric acid: it forms fine greenish needles. Hydrate of baryta did not decompose this salt so as to isolate the base. The salt is more readily soluble in hot than in cold water, and may therefore be purified by recrystallization. Analysis:—

Iridium	45·64	..	1 =	1233·20	45·65
Chlorine	16·37	16·38	1	443·20	16·40
Hydrogen	2·84	..	6	75·00	2·77
Nitrogen	..	..	2	350·00	12·45
Oxygen	..	..	1	100·00	4·22
Sulphuric acid..	18·46	18·35	1	500·00	18·51

Muriate of the Iridium Base, $IrCl\,N^2\,H^6, Cl$, makes its appearance, when the nitrate is treated with muriatic acid, in the form of a violet precipitate, which is very sparingly soluble in cold, but dissolves pretty readily in hot water, separating again from this solution on cooling in violet crystals. Nitrate of silver throws down half the chlorine from the solution. Analysis:—

Iridium.....	48·38	1 =	1233·20	48·46
Chlorine	34·87	2	886·40	34·86
Ammonia	16·72	2	425·00	16·68

This salt consequently differs from all the preceding in containing no oxygen. With the same quantity of hydrogen, it contains twice as much chlorine. The oxygen must therefore have formed water with the hydrogen, which was expelled during the combination.

New Base, $IrO\,NH^3$.—Oxide of ammonium, in which 1 equiv. of

hydrogen is replaced by 1 equiv. of iridium. By means of heat, diluted sulphuric acid changes the yellow salt, $IrCl\,NH^3$, into a new base free from chlorine, with evolution of muriatic acid. The new salt crystallizes in large orange-yellow laminæ, which are readily soluble both in cold and hot water. This sulphuric acid salt gave on analysis—

Iridium	60·43	1 =	1233·20	60·57
Ammonia.....	10·39	1	212·50	10·43
Sulphuric acid.....	24·45	1	500·00	24·52
Oxygen	..	1	100·00	4·48

Biammoniacal Protochloride of Iridium, $IrCl\,N^2\,H^6$.—The yellow salt $IrCl\,NH^3$ is heated in a flask with ammonia, replacing the ammonia lost by evaporation. At first, on cooling, this salt is deposited unchanged, but afterwards a new compound separates in the form of a white precipitate. By continued boiling with an excess of ammonia, the yellow salt is by degrees entirely changed into the whitish substance. With alkalies in the cold this substance evolves no trace of ammonia, and but little even when heated. Analysis:—

Iridium	57·13	58·24	1 =	1233·20	58·68
Chlorine	20·53	20·71	1	443·20	20·09
Ammonia	20·95	20·51	2	425·00	20·23

A New Base, $IrO\,N^2\,H^6$, is obtained in combination with sulphuric acid, by treating the preceding compound with sulphuric acid of moderate strength. Muriatic acid escapes, and the resulting new salt crystallizes in rhombic prisms. It is purified by recrystallization. The sulphate dissolves readily in boiling water; it is soluble with difficulty in cold water, and scarcely at all in alcohol. Analysis of the salt $IrO\,N^2\,H^6$, SO^3 gave:—

Iridium	54·75	54·67	54·65	1 =	1233·20
Ammonia	..	18·76	18·74	2	425·00
Sulphuric acid	22·17	22·14	22·11	1	500·00
Oxygen	..	..	..	1	100·00

The nitrate of the same base, $IrO\,N^2\,H^6$, NO^5, is obtained by the double decomposition of the preceding salt with nitrate of baryta. It forms yellow needles, which are readily soluble both in hot and cold water, melt when heated, and then suddenly become decomposed with flame. It may also be obtained directly from the compound $IrCl\,N^2\,H^6$ by heating it with nitric acid.

The new compound first described (*ammoniacal protochloride of iridium*), $IrCl\,NH^3$, furnishes, according to the preceding observations—

1, with sulphuric acid, the base $IrO\,NH^3$;
2, with nitric acid, the base $IrCl\,N^2\,H^6\,O$;
3, with ammonia, the compound $IrCl\,N^2\,H^6$;
4, this, with sulphuric acid, the base $IrO\,N^2\,H^6$.

Bull. de St. Pétersb. Chem. Phys. Math., Cl. xi. p. 25.

Note upon Azobenzide and Seminaphthalidine. *By* N. ZININ.

Azobenzide becomes readily transformed into benzidine when its alcoholic solution is treated with sulphurous acid, the sulphate of that base, which is almost insoluble, being then immediately thrown down.

Azobenzide is readily changed into benzidine by the treatment of its alcoholic solution with reducing agents.

The author has prepared seminaphthalidine in a perfectly colourless form by repeated alternate crystallizations from alcohol and water. The long acicular crystals are very shining when formed in alcohol. The sulphate of this base is less soluble in water than the base itself; it crystallizes in small scaly crystals of a white colour. On analysis it gave 38·20 per cent. of sulphuric acid; the formula $C^{10} H^5 N, SHO^4$ requires 38·28 per cent. The copper-red colour of the base arose from a small admixture of another brownish-red substance, which is much more readily soluble in alcohol than seminaphthalidine. This colouring matter crystallizes from its watery solution in fine, dull, acicular crystals, which, when heated in a glass tube, first melt into a red fluid, and then distil with partial decomposition, but without deflagration.—*Bull. de St. Pétersb. Phys. Math.*, Cl. x. p. 348.

On the Chemical Constitution of Wines. *By* F. L. WINCKLER.

The author has already shown that the essential constituents of grape-wine are alcohol, œnanthic æther, tartrate of potash combined with a minute quantity of tartrate of lime, free tartaric acid and a kind of extractive substance very readily oxidizable; while cider, when it has not been kept in casks containing tartar, generally contains no tartrate of potash, but free lactic acid, a considerable quantity of lactate of lime, alcohol and vegetable mucilage, the latter substance being in larger quantity the younger the cider is.

Moreover, it is known, with regard to the grape-wines, that they deposit the greater part of the tartrate of potash during the fermentation, the separation of the ferment and the first period of the cellaring; while, on the contrary, older wines, which have laid for some time in casks containing tartar, take up again no inconsiderable quantity of tartar, and for that reason give a precipitate when mixed with alcohol; they generally yield less alcohol, and have a stronger acid reaction than new wines. The inferior wines generally produced in 1851, presented a great uniformity in their physical and chemical characters; they were very acid in November, afterwards pale yellow; the taste was strongly though not unpleasantly acid, and purely vinous; they all contained a somewhat large quantity of free carbonic acid.

For the first experiments, an inferior kind of wine, made from white grapes grown in the neighbourhood of Bensheim in the Bergstrasse, was selected. The specific gravity was 1·0021 at 57°·2 F.; the per-centage of alcohol, 4·8. Mixed with 2 vols. of alcohol, a

little tartar separated. On the addition of neutral tartrate of potash, a considerable quantity of tartar was separated, and besides this a soluble salt was formed.

On distillation, a very pure alcohol was obtained, possessing a very agreeable odour of œnanthic æther. The residue contained 60 grs. of acetate of potash. From this residue, when evaporated to a brown syrup, about 14 drms. of tartar separated, besides the salt of an acid, which, from its resemblance to citric acid, the author calls paracitric acid. The acid liquid separated from the saline mass was saturated with carbonate of soda, 20 oz. of which were required. This solution could not be decolorized by means of animal charcoal; it was strongly acidulated with acetic acid, acetate of lead added as long as any precipitate was formed, this lead precipitate decomposed by sulphuric acid, the acid liquor saturated with carbonate of soda, treated with animal charcoal, and precipitated again with acetate of lead, by which means 15 oz. of a lead salt were obtained. This quantity of salt was again decomposed by sulphuric acid, the liquor treated with sulphuretted hydrogen and evaporated to dryness, by which means a pale yellowish transparent syrup was obtained, which after some time became crystalline. This acid is the one contained in the above-mentioned soluble salt. The paracitric acid crystallizes in most cases with difficulty from the concentrated aqueous solution, frequently requiring some months; the crystallization is more rapid at a moderately-elevated temperature. The crystals are described as corresponding exactly in form with those of grape-sugar; they are colourless, transparent, rhomboidal prisms, with a remarkable vitreous lustre. When small quantities of the acid crystallize in cylindrical tubes, it forms arborescent masses. The acid is soluble in water in almost every proportion, very soluble in cold alcohol, slightly in æther. The sparing solubility in æther distinguishes it from citric acid; its behaviour with lime-water and chloride of calcium distinguishes it from tartaric, racemic and malic acids; when a solution of the acid (not too dilute) is supersaturated with lime-water, it remains clear until heated to near the boiling-point, when a white precipitate of paracitrate of lime is thrown down. The neutral paracitrates precipitate chloride of calcium only by the aid of heat. The author considers that paracitric acid possesses the physical characters of malic acid united with the chemical characters of citric acid.

Acid Paracitrate of Ammonia, prepared by saturating half of a solution of the acid, adding the remainder, and evaporating to the consistence of a syrup; after several days or weeks, crystals are formed having a vitreous lustre and the form of cane-sugar. By spontaneous evaporation, the salt crystallizes in bunches of prisms like mannite.

The Neutral Potash or Soda Salts can with difficulty be obtained in crystals; the acid potash salt readily forms four-sided prisms; it is readily soluble in water, slightly in alcohol; the solution has a strong acid taste.

Neutral Paracitrate of Magnesia was obtained by saturating the

acid with carbonate of magnesia. It forms short prisms with many terminal planes, is slightly soluble in cold water, abundantly in hot, insoluble in alcohol. If the solution is rapidly evaporated to dryness, a transparent amorphous mass remains, which, when dissolved in water and slowly evaporated, again forms the usual crystals. The salt is unaltered by exposure to the air; it loses its water of crystallization between 300° and 392° F. Analysis gave the numbers under I. II. shows the composition of basic citrate of magnesia :—

	I.	II.
Magnesia	17·00	17·52
Acid	53·70	46·88
Water	29·30	35·60

The principal difference is in the per-centage of water.

Paracitrate of Lead, prepared by adding to a very dilute solution of the neutral soda salt, slightly acidulated with acetic acid, a sufficient quantity of oxide of lead, and then leaving the boiling filtered solution in a cold place. After some time the salt crystallizes in beautiful groups of crystals, similar to sulphate of quinine; it has a considerable lustre, is almost insoluble in cold water, and sparingly soluble in boiling water. When prepared at the ordinary temperature from concentrated solutions, it has the form of a scaly caseous precipitate, which separates very quickly, and when dried is a pulverulent brilliant mass. Between 158° and 176° F. some of the salt frequently agglutinates to a viscous transparent mass, while the rest remains dry.

Paracitrate of Silver, prepared in the same way as the lead salt. It is white, pulverulent, and quite as sensitive to the influence of light as chloride or citrate of silver. It is distinguished from the latter by its decomposition at a high temperature, at first melting imperfectly, then inflaming and burning with a blue flame like alcohol; the silver remains as a porous, homogeneous, dull mass. For the sake of comparison, the author prepared in the same way the citrate, tartrate and paracitrate of silver; dried at 158° F., they lost no water. Analysis gave for each—

	I.	II.	III.
Acid	36·60	37·630	36·60
Oxide of silver	63·40	62·370	63·40

Consequently the paracitrate contains the same constituents as the citrate.

Paracitrate of Zinc.—The physical characters of this salt vary with the mode of preparation. When carbonate of zinc is dissolved to saturation in a moderately-concentrated solution of the acid, short four-sided prisms with a vitreous lustre are obtained. The salt is abundantly soluble in water, insoluble in alcohol, and tastes faintly metallic like lactate of zinc. Dried in the air at 158° F., it lost its water of crystallization, and gave on analysis—

Acid	63·00
Oxide of zinc	31·50
Water	5·50

When saturated solutions of paracitrate of soda and sulphate of zinc are mixed in quantities corresponding with the above analysis, and allowed to stand for a while in tall vessels, a gelatinous precipitate is deposited, which becomes crystalline when dried in the air, at the same time losing water; its composition is then the same as the above salt. Dried upon bibulous paper, it has the following composition*:—

Acid	24·0
Oxide of zinc	12·5
Water	64·0

The author infers from these data that the difference between citric and paracitric acids consists in their relation to water, and that as paracitric acid is contained in the wine made from unripe grapes, while this acid is not present in the juice of thoroughly-ripened grapes, it must be converted into sugar during the ripening.

Winckler likewise examined another wine of the same year, from the neighbourhood of Monsheim, and not much unlike the above. Its specific gravity was higher, and the per-centage of alcohol 4·4. The constituents of this wine proved to be different, and it was likewise found that the influence of the soil affected the composition of the wines of the same year. The examination was carried out in the same manner; the quantity of acetic acid was so small as to be scarcely recognisable; but the acid residue left on distilling 34 lbs. of wine contained a larger quantity of tartar (20½ drms.), and such a large quantity of a gummy substance, that Winckler thought it necessary, after separating the tartar, to mix it with alcohol before treating it with soda and a lead salt. By this means a considerable quantity of a thick magma of dark brown colour was separated, which was insoluble in alcohol. It was washed with alcohol, and then dissolved in water, upon which a minute quantity of tartar and paracitrate of potash separated. By reprecipitation with alcohol, a gummy substance of dark colour, but soluble in water, was obtained, which when dried in a water-bath weighed just 2 oz., and showed all the reactions of gum.

The acid liquid left after the first treatment with alcohol was then employed for the preparation of paracitric acid, of which however a smaller quantity was obtained than from the former wine.

The Bergstrasser wine which had laid eight months was then examined. It was found to have lost ½ a per cent. of alcohol; acetic acid was altogether absent; the quantity of paracitric acid was quite unaltered, but the distillate of 72 lbs. of the wine yielded on rectification over carbonate of potash ½ an ounce of pure butyrate of potash.

The Bouquet of Wine.—Winckler states that the odour of wine depends upon the presence of a compound of a volatile organic acid with a volatile base; this compound always contains nitrogen†, and has a different smell in different wines. The following method of isolating these substances was adopted. From 2 to 4 lbs of wine

* According to Held, tribasic citrate of zinc is anhydrous, and contains 39·42 per cent. of ZnO.

† In the acid or the base?

were evaporated in a water-bath to the consistence of syrup, in order to separate the alcohol, œnanthic æther and greater part of the water; the residue was dissolved in 3 or 4 oz. of water, and poured over an equal weight of coarsely-powdered caustic lime in a capacious tubulated retort, previously furnished with a condenser and a capacious receiver with a safety-tube, and the whole fitted air-tight. When fresh lime is used, the formation of hydrate takes place in a very short time without the application of heat, and meanwhile there distils over a volatile very limpid liquid, with a strong alkaline reaction, and a peculiar, very agreeable odour. This substance may be completely neutralized by acids, and the solution of the salt thus obtained possesses in a high degree the peculiar *bouquet* of the wine. The residue of the distillation was treated with water when cold, the filtered liquid evaporated, and distilled with the requisite quantity of bisulphate of potash. The distillate was an acid, which when mixed with the volatile base formed a neutral salt, and was in short the substance to which the bouquet of the wine was owing.

Winckler treated beer in a similar manner with caustic lime, and obtained a strongly basic ammoniacal distillate smelling of beer and hops. He also obtained a distillate exactly like it by distilling well-washed beer-yeast with lime: the yeast employed to set up the fermentation, on the contrary, yielded scarcely a trace of this nitrogenous compound when treated with lime, showing that it passes into the beer during the fermentation.

The formation of bases by the action of caustic lime upon vegetable juices was likewise attempted with aqueous extracts of ergotized corn, dandelion root, couch-grass root, corn poppy, camomile, peppermint, the sap of fresh elder roots, aloe bitter free from resin, the aqueous solutions of extracts of dandelion, fumitory, couch root and wormwood. All the bases formed from these substances by means of caustic lime were, in a hydrated state, volatile, colourless liquids, giving a strong alkaline reaction with litmus. Their origin is readily indicated by their smell. The acids formed simultaneously are analogous to the acetic, butyric, &c.; all possess a peculiar, and many a similar smell, in no way indicating their origin; they form with bases salts, whose chemical behaviour distinguishes the greater number of these acids as peculiar. Combined with their corresponding bases, they form compounds possessing in a high degree the odour of the substances from which these products are obtained.

By distilling the dry substance of decayed potatoes with caustic lime, nicotine is obtained; and by distilling musk with lime, a volatile base is obtained, which, combined with the acid retained by the lime, yields a substance possessing exactly the smell of musk.—*Jahrb. für Prakt. Pharmacie*, xxv. 65–84.

Remedy for the Stings of Bees. By M. Gumprecht.

The stung place is to be rubbed with the freshly-pressed juice of the honeysuckle (*Lonicera caprifolium*). The expressed juice may be kept in closely-stoppered bottles for this purpose.—Dingler's *Polyt. Journ.*, cxxvi. p. 80.

ANALYTICAL CHEMISTRY.

Apparatus for the Determination of Carbonic Acid.

By MAX. SCHAFFNER.

THIS is a modification of the apparatus of Will and Fresenius, which may be weighed on delicate balances, and admits of the determination of carbonic acid with very great accuracy, even when but small quantities of the substance to be examined can be employed. The figure shows it in natural size.

A is a tube into which the substance is introduced and weighed. It is then moistened with a little water, and the tube closed with a cork, *c*, through which pass two tubes, *g* and *r*, *g* passing through the cork *d* closing the tube B, which is filled with concentrated sulphuric acid as far as is shown in the figure. The tube *g* is closed by a piece of glass rod *s* fitting into a caoutchouc tube *k*. The tube *i* is to allow the escape of the carbonic acid disengaged. The whole apparatus may be hung on the balance by the wire hook *h*.

When thus arranged and weighed air is drawn through *i*, the acid rises through the tube *r* to the substance, and the carbonic acid disengaged is dried by passing through the sulphuric acid. When the effervescence has ceased, the glass rod *s* is taken out, and air drawn through the apparatus at *i* to remove all the carbonic acid. It is now weighed again, and the loss of weight gives the quantity of carbonic acid.—*Ann. der Chem. und Pharm.*, vol. lxxxii. p. 335.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 10, 1852.

"On a new Series of Organic Bodies containing Metals." By Dr. E. Frankland, Professor of Chemistry, Owen's College, Manchester.

The author communicates in this memoir the continuation of his researches, a preliminary announcement of which appeared several years ago, upon a new series of organic compounds closely allied to cacodyle in their composition and properties, and which, like that body, are formed by the union of the alcohol radicals with various metals, and are distinguished for their powerful electro-positive character. These remarkable compounds are procured by the action of heat or light upon their proximate constituents, and are thus distinguished from most other organic compounds of this nature by the manner of their formation. The author describes seven of these compounds.

Stanethylium.—When iodide of ethyle and metallic tin are exposed to the influence of heat or light, which is most conveniently done in sealed glass tubes, the tin gradually dissolves in the ethereal liquid, which finally solidifies to a mass of colourless crystals. A quantity of gas, comparatively very small, is generated at the same time. This gaseous product of the reaction proved, on analysis, to be a mixture of hydride of ethyle and olefiant gas, produced from the decomposition of iodide of ethyle by tin into iodide of tin and ethyle, which last is transformed at the moment of its liberation into the two gases just mentioned. The principal and most important reaction, however, consists in the direct union of tin with iodide of ethyle, giving rise to a crystalline body which is the iodide of a new organic radical, *stanethylium*.

By double decomposition the other compounds of stanethylium can be readily formed; the author has prepared and described the oxide, chloride, bromide and sulphide of stanethylium; these bodies exhibit a striking resemblance to the corresponding bi-compounds of tin, but are distinguished from them by a peculiar pungent and irritating odour resembling that of the volatile oil of mustard.

If a slip of zinc be immersed in a solution of chloride of stanethylium, dense oily drops soon form on the surface of the zinc, and finally collect at the bottom of the vessel. This oily liquid is the radical stanethylium, which possesses the following properties:—it exists at ordinary temperatures as a thick heavy oily liquid of a yellow or brownish-yellow colour, and an exceedingly pungent odour resembling that of its compounds, but much more powerful. It is insoluble in water, but soluble in alcohol and ether. At about 150° C. it enters into ebullition, but is simultaneously decomposed, metallic tin being deposited. In contact with air stanethylium rapidly absorbs oxygen, and is converted into oxide of stanethylium. Chloride, iodide and bromide of stanethylium are instantaneously formed by the action of chlorine, iodine and bromine, or their hydrogen acids respectively, upon stanethylium. The two first are in

every respect identical with the salts above mentioned, and the identity of the bromide is further proved by an ultimate analysis. The formula of stanethylium is $C_4 H_5 Sn$; that of the oxide $C_4 H_5 SnO$, and that of the bromide $C_4 H_5 Sn Br$. Stanethylium therefore perfectly resembles cacodyle in its reactions, combining directly with the electro-negative elements, and regenerating the compounds from which it has been derived.

Stanmethylium and stanamylium are formed when the iodides of methyle and amyle respectively are exposed to the action of light in contact with tin; their salts are isomorphous with those of stanethylium, but they have not yet been completely investigated.

Zincmethylium.—This radical is formed in an uncombined state when iodide of methyle and zinc are exposed to a temperature of about 150° C. in a sealed tube; the zinc gradually dissolves with an evolution of gas, whilst a mass of white crystals and a colourless mobile liquid refracting light strongly, occupy, after a few hours, the place of the original materials. In this reaction two distinct decompositions take place, viz. the decomposition of iodide of methyle by zinc with the production of iodide of zinc and liquid zincmethylium, and the decomposition of iodide of methyle by zinc with the formation of iodide of zinc and the gaseous radical methyle. The zincmethylium was obtained pure by distillation in an atmosphere of dry hydrogen. Its formula is $C_2 H_3 Zn$, and it possesses the following properties. It is a colourless, transparent and very mobile liquid, possessing a peculiar penetrating and insupportable odour, and boiling at a low temperature. Zincmethylium combines directly with oxygen, chlorine, iodine, &c., forming somewhat unstable compounds. Its affinity for oxygen is even more intense than that of potassium; in contact with atmospheric air it instantaneously ignites, burning with a beautiful greenish blue flame, and forming white clouds of oxide of zinc; in contact with pure oxygen it burns with explosion, and the presence of a small quantity of its vapour in combustible gases gives them the property of spontaneous inflammability in oxygen. Thrown into water, zincmethylium decomposes that liquid with the evolution of heat and light; when this action is moderated, the sole products of the decomposition are oxide of zinc and hydride of methyle.

The extraordinary affinity of zincmethylium for oxygen, its peculiar composition, and the facility with which it can be procured, cannot fail to cause its employment for a great variety of transformations in organic compounds; by its agency there is every probability that oxygen, chlorine, &c. can be replaced atom for atom by methyle, and thus entirely new series of organic compounds will be produced, and clearer views of the rational constitution of others be obtained.

The gaseous methyle formed simultaneously with zincmethylium is identical in composition and properties with the methyle derived from the electrolysis of acetic acid; it was mixed, however, with hydride of methyle generated by the decomposition of accompanying zincmethylium vapour by the water over which the gas was collected.

Zincethylium and zincamylium are homologous bodies formed by similar processes; their investigation is not yet completed.

Hydrargyromethylium.—The author has only yet studied the iodide of this radical, which is formed by the action of sunlight upon iodide of methyle and metallic mercury. After an exposure of several days to sunlight, white crystals begin to form in the liquid, which finally solidifies to a white crystalline mass; ether dissolves out the new compound and deposits it perfectly pure by spontaneous evaporation

Iodide of hydrargyromethylium ($C_2 H_3 HgI$) is a white solid, crystallizing in minute nacreous scales, which are insoluble in water, moderately soluble in alcohol, and very soluble in ether and iodide of methyle; it is slightly volatile at ordinary temperatures, and exhales a weak but peculiarly unpleasant odour, which leaves a nauseous taste upon the palate for several days. At 100° C. the volatility is much greater, and the crystals are rapidly dissipated at this temperature when exposed to a current of air. At 143° C. it fuses and sublimes without decomposition, condensing in brilliant and extremely thin crystalline plates. In contact with the fixed alkalies and ammonia it is converted into oxide of hydrargyromethylium, which is dissolved by an excess of all these reagents.

A corresponding compound containing amyle is formed, though with difficulty, under similar circumstances, but the attempts to form one containing ethyle have not yet been successful. Preliminary experiments have also been made with other metals, amongst which arsenic, antimony, chromium, iron, manganese and cadmium promise interesting results.

From a review of the composition and habits of all the organo-metallic bodies and their compounds at present known, the author is of opinion that the view most generally held respecting the constitution of cacodyle, according to which that radical is a conjugate compound consisting of arsenic conjugated with two atoms of methyle, and which view must, if true, be applied to all the organo-metallic bodies, is no longer tenable; and he contends that the behaviour of these bodies clearly indicates that they are compounds formed upon the type of the oxides of the respective metals, a portion of the oxygeu being replaced by the several radicals, methyle, ethyle and amyle; the establishment of this new view of their constitution will remove these bodies from the class of organic radicals, and place them in the most intimate relation with ammonia and the bases of Wurtz, Hofmann and Paul Thenard; indeed the close analogy between stibethine and ammonia first suggested by Gerhardt, has been most satisfactorily demonstrated by the behaviour of stibethine with the haloid compounds of methyle and ethyle. Stibethine furnishes us therefore with a remarkable example of the law of symmetrical combination, and shows that the formation of a five-atom group from one containing three atoms can be effected by the assimilation of two atoms, either of the same or of opposite electro-chemical character: this remarkable circumstance suggests the following question. Is this behaviour common also to the corresponding compounds of arsenic, phosphorus and nitrogen, and can the position of each of the five atoms with which these elements respectively combine be occupied indifferently by an electro-negative or an electro-positive element? This question, so important for the advance of our knowledge of the organic bases and their congeners, cannot now long remain unanswered.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Mutton-fat. By Dr. Heintz.

The method adopted by the author for the separation of the fatty acids obtained by the saponification of this fat, was essentially the same as that employed by him in the investigation of human fat, which has already been communicated*. In the partial precipitation of the fatty acids, however, he no longer employed acetate of lead, but partly acetate of baryta and partly acetate of magnesia.

In the products of the saponification of human fat, Heintz stated that he had found an acid melting at 156° F., which he regarded as identical with stearophanic acid, another acid, melting at 138° F. and crystallizing in laminæ, anthropic acid, together with margaric and palmitic acids, oleic acid and another fluid acid, and glycerine. At the commencement of the investigation, mutton-fat appeared to furnish results exactly similar to those obtained with human fat. Its fluid portion especially is composed exactly like that of human fat, that is to say, it contains, besides oleine, another fat, which by saponification furnishes an acid possessing a much lower atomic weight than oleic acid, and the baryta salt of which is much more difficult of solution in alcohol than that of oleic acid, but on the other hand much more soluble in æther.

The solid fatty acids of mutton-fat, when separated by the above method, exhibited exactly the same phænomena as those of human fat, except only that the quantity of the acid fusible at 156° F. and of anthropic acid appeared here to be much greater. It was therefore to be hoped that they might in this case be obtained in sufficient quantity to enable their nature to be ascertained. These two acids existed in the first portions of the acids separated by acetate of magnesia. The last portions consisted apparently of margaric and palmitic acids. Heintz has proved particularly the existence of palmitine in mutton-fat.

The acid melting at 156° F. must henceforward bear the name of stearic acid, as it is evidently the acid prepared by Chevreul from mutton-fat, and so named by him. This acid however does not melt at 150° F., as stated by Chevreul, but at 156°·56 F.; it has also a different composition from that given by Redtenbacher, having the formula of stearophanic acid, $C^{36}H^{35}O^{3}+HO$. Several ana-

* Chem. Gaz., vol. ix. p. 361.

lyses of the acid itself, as well as of its lead, silver, copper, baryta, magnesia and soda salts, and lastly of stearic æther, agree very exactly with this formula. Moreover, if the results of Redtenbacher's analyses of stearic acid be calculated with 75 as the atomic weight of carbon, his numbers will also agree very well with the calculation according to the above formula.

On closer examination of the portion of acid, which, to judge from its melting-point and its faculty of crystallizing on cooling in large laminæ, must contain anthropic acid, Heintz obtained unexpected results. When this portion of acid was separated according to the method formerly described into four separate portions by means of acetate of baryta, the two first portions furnished, even by the first recrystallization, an acid fusing at above 140° F., their own melting-point being 131° F.; from this stearic acid could readily be obtained by further recrystallization. The third portion also, by frequent recrystallizations, passed over at last into an acid with its melting-point above 140° F.; the fourth gave margaric acid by this process. When that part of the third portion which remained in the alcoholic solution after the recrystallizations, and which must therefore consist essentially of anthropic acid, was separated according to the process stated in four portions, the separate portions behaved, on recrystallization from alcohol, exactly as the first time; in this case also the first and second portions passed over into stearic acid; the third, the same, but with more difficulty, whilst the fourth furnished margaric acid. When, lastly, the portion remaining dissolved in the alcohol was similarly treated for the third time, the results were exactly the same. The fact that no pure anthropic acid, not decomposable into different substances, could be obtained in this manner, convinced Heintz that this acid must be a mixture of margaric and stearic acids. Gottlieb had already observed, that a mixture of margaric and stearic acids in certain proportions possesses a lower melting-point than even margaric acid. The circumstance that anthropic acid melts at 133° F. does not therefore militate against the supposition that it may be a compound. Heintz now endeavoured to prepare an acid possessing the properties of anthropic acid, by fusing together margaric and stearic acids. In this he succeeded perfectly. A mixture of 3 parts of stearic acid with 5–6 parts of margaric acid melts at 133° F., and crystallizes on solidifying in fine large laminæ. The same phænomenon took place, however, when 6 parts of pure palmitic acid, melting at 144° F., were fused with 4 parts of stearic acid. It was remarkable that this mixture possessed exactly the same properties as that before mentioned. Its melting-point was 133° F.; and if the proportions of this mixture be observed, it will be seen that somewhat less margaric acid than palmitic acid is required to give the properties of anthropic acid to stearic acid. This led Heintz to think that margaric acid might be nothing but a mixture of a large quantity of palmitic acid with a little stearic acid. Direct experiment perfectly confirmed this supposition. When about 1 part of stearic acid was mixed with 9–10 parts of palmitic acid, a compound was produced which melted at

140° F., solidified on cooling into a mass of entangled needles, and possessed all the properties of margaric acid. This experiment was several times repeated, and always with the same result, whether the acids had been obtained from human fat, mutton-fat or spermaceti. Moreover, when a large quantity of margaric acid obtained from mutton-fat, which no longer appeared to change its melting-point by recrystallization, and was therefore considered pure, was submitted to the action of acetate of baryta, it was also shown that this acid was a mixture from which palmitic acid at least could be obtained. The fatty acid contained in the baryta salt first thrown down melted at 135°·5 F., solidified without crystallizing, and was evidently a mixture of more stearic and less palmitic acid than is contained in the supposed margaric acid. The other portion crystallized in long needles, but only melted at 140°·45. By repeated crystallizations, the melting-point was raised to 142°·7 F., and would certainly have reached 144° F., had not the small quantity of acid remaining prevented further recrystallizations. Its properties were exactly those of palmitic acid. It no longer crystallized in needles, but in scales like palmitic acid.

According to the above results, it is very evident why the analysis of margaric acid gives results corresponding with the formula $C^{34} H^{34} O^4$; for it is exactly a mixture of $C^{36} H^{36} O^4$ (stearic acid) and $C^{32} H^{32} O^4$ (palmitic acid). All previously known phænomena are thus explained in a simple manner. Only one still remains for explanation, and that is, why direct mixture, and indeed only certain mixtures of stearic and palmitic acids, crystallize so beautifully. For the explanation of this phænomenon, the fact is necessary that a mixture of about 1 part of stearic and 2 parts of palmitic acid melt at about 131° F. This mixture may be fused with more palmitic or more stearic acid, and both these mixtures have a higher melting- and solidifying-point than the former. If, therefore, such a mixture be cooled gradually, the excess of palmitic or stearic acid first separates in crystals, and the original mixture solidifies at last only at 131° F. The form of the first-found crystals is however not changed. In fact, the form in which stearic acid shoots its crystals in a dilute alcoholic solution is that of broad laminæ, whilst palmitic acid crystallizes from alcohol in fine needles. Thus in anthropic acid the stearic acid crystallizes in laminæ from its solvent, which only becomes solid at 131°; whilst the palmitic acid crystallizes in needles out of margaric acid under similar circumstances.

According to this, neither margaric nor anthropic acid exist, if by these names be understood a chemically-pure acid. Both are only mixtures of stearic and palmitic acids in different proportions. Human fat, therefore, when its fluid portion is removed, consists only of palmitine and stearine, both which fats are also contained in mutton-fat, although in different proportions. In this case the stearine greatly exceeds the palmitine. Spermaceti, moreover, contains neither margæthal nor stearophæthal, as was formerly stated by Heintz, but only stearæthal, or the compound of stearic acid and

oxide of cetyle, together with palmæthal, cetæthal, myristæthal and cocæthal.

In conclusion, it is to be observed, that margaric acid can scarcely be changed in its composition by recrystallization, because the two acids of which it is composed are soluble in alcohol in about the same proportions in which when mixed they form the acid with the properties of margaric acid. On the other hand, anthropic acid, when separated by means of acetate of baryta in such a manner that it may be divided into two nearly equal portions, does not furnish two acids of essentially different melting-points. It is therefore more readily ascertained that this is a mixture by recrystallization from alcohol; while the margaric acid requires partial precipitation with acetate of baryta to show this.—*Bericht der Akad. der Wissensch. zu Berlin*, August 1852, p. 540.

Examination of the Leaves of Rhododendron ferrugineum. *By* R. Schwartz.

Rhodotannic Acid, $C^{14} H^6 O^7$.—If the leaves of *Rhododendron ferrugineum* be extracted with alcohol, the alcohol distilled from the green decoction on the water-bath, and the residue mixed with water and put upon a filter, a pale yellow fluid is obtained, whilst a green mixture of wax, resin, fat, and chlorophylle remains upon the filter. The filtered liquid, which acquires a strong green colour on the addition of salts of peroxide of iron, gives with a solution of acetate of lead a yellow precipitate, which, when dilute acetic acid is poured over it, dissolves with a golden-yellow colour, leaving behind it a greenish-yellow mass. This solution being filtered and heated to boiling, an excess of tribasic acetate of lead is added to it. A precipitate of a beautiful chrome-yellow colour is formed, which may be dried at 212° F. without undergoing any change. The analysis of the precipitate so dried gave—

Carbon	28·20	42 =	252·000	28·21
Hydrogen	2·28	19	19·000	2·13
Oxygen	19·57	22	176·000	19·70
Oxide of lead	49·95	4	446·952	49·96

$$C^{42} H^{19} O^{22}, 4PbO = 3(C^{14} H^6 O^7, PbO) + PbO, HO.$$

Rhodotannic acid in the anhydrous state has therefore the composition represented by the formula $C^{14} H^6 O^7$. If the lead salt obtained in this manner be decomposed under water by sulphuretted hydrogen, the fluid heated to boiling with the sulphuret of lead and filtered whilst boiling hot, a dark yellow solution of pure rhodotannic acid is obtained, from which this acid may be prepared by driving off the water in the chloride of calcium bath in a stream of carbonic acid gas. When pounded, it forms an amber-yellow powder, of an acid astringent taste. After trituration it was placed *in vacuo* over sulphuric acid. The two following analyses were performed with acid prepared at two separate operations:—

Carbon.....	54·81	55·01	56 = 336	55·00
Hydrogen	4·64	..	27 27	4·41
Oxygen	40·55	..	31 248	40·59

$C^{56} H^{27} O^{31} = 3(C^{14} H^{7} O^{8}) + C^{14} H^{6} O^{7}$ or $4(C^{14} H^{6} O^{7}) + 3HO$.

The watery solution of rhodotannic acid behaves towards chloride of tin exactly like callutannic acid. The tin salt is of a fine yellow colour, and may be dried at 212° F. without decomposition. Analysis gave—

Carbon	22·39	140 =	840·0	22·61
Hydrogen	2·96	87	87·0	2·34
Oxygen	20·42	97	776·0	20·89
Peroxide of tin	54·23	27	2025·0	54·16

$C^{140} H^{87} O^{97}, 27SnO^{2} = 10(C^{14} H^{8} O^{9}, 2SnO^{2}) + 7(SnO^{2}, HO)$.

The result of the analysis also agrees very well with the formula $C^{14} H^{9} O^{10}, 3SnO^{2}$. The aqueous solution of pure rhodotannic acid, when heated with mineral acids, gives a reddish-yellow precipitate, in the impure state a reddish-brown one. The substance obtained from the impure acid has all the properties and the same composition as phlobaphene. That procured from the pure acid, to which the author gives the name of *rhodoxanthine*, is prepared in the same way as calluxanthine, with which it is very analogous in its properties: it was dried *in vacuo* over sulphuric acid, and then employed for analysis:—

Carbon.....	52·40	28 =	168	52·66
Hydrogen.....	4·66	15	15	4·70
Oxygen.....	42·94	17	136	42·64

$C^{18} H^{15} O^{17} = C^{14} H^{7} O^{8} + C^{14} H^{8} O^{9}$ or $2(C^{14} H^{6} O^{8}) + HO$.

The 1 equiv. of water was evidently expelled at 212° F., but at this temperature the substance was so changed in appearance that it was necessary to desist from drying it at a higher temperature.

If the leaves of the *Rhododendron ferrugineum* be extracted with water in a retort, there passes over with the vapour of water an oil of a peculiar but not unpleasant smell; this belongs to that numerous class of oils which contain carbon and hydrogen in the same proportion as oil of turpentine.

The oil is contained in very small quantity in the leaves of *Rhododendron ferrugineum*, so that it was not possible to undertake any further investigation of it. It is of a light yellow colour; by distillation with anhydrous phosphoric acid, it becomes colourless, and acquires an odour similar to that of oil of turpentine. The following analyses were made with such oils, after drying them over chloride of calcium:—

Carbon.....	84·19	80 =	480	84·51
Hydrogen.....	11·22	64	64	11·26
Oxygen.....	4·59	3	24	4·23
Carbon	85·85	80	480	85·71
Hydrogen.....	11·73	64	64	11·43
Oxygen	2·42	2	16	2·86

In the watery decoction of the leaves another acid is contained besides the rhodotannic acid; this gave all the reactions of citric acid, but could not be obtained in a crystallized state. There are also in the watery decoction inconsiderable quantities of ericoline and of some dark-coloured products of the oxidation of the rhodotannic acid.

In the water which goes over with the essential oil during the extraction of the leaves of *Rhododendron ferrugineum* in a distillatory apparatus, very small quantities of fatty acids are contained. If the water be saturated with carbonate of soda and the fluid evaporated, there remains a saline residue, which, when moistened with sulphuric acid, evolves the odour of acetic or formic acid, as well as that of butyric acid.—*Bericht der Akad. der Wissensch. zu Wien*, July 1852.

On the Compounds formed by some Essential Oils with the Alkaline Bisulphites. *By* C. BERTAGNINI.

Having already ascertained the formation of a compound of nitrated oil of bitter almonds with sulphites, I have examined whether the oil of bitter almonds was capable of forming an analogous compound with the alkaline sulphites. This conjecture has been confirmed by experiment.

Extending this view, I have endeavoured to form similar compounds with other essential oils.

I have operated upon a considerable number of these. Thus I have submitted to the action of the alkaline sulphites, the hydrurets of benzoyle, salicyle, anisyle, cinnamyle, and of cuminyle, the œnanthylic and capric aldehydes, and the essential oils of lavender, aniseed, valerian, citron, cedar, carraway, juniper, coriander, myrtle, fennel, marjoram, savin, Gualteria, neroli, parsley, nutmeg, pimento, sassafras, chamomile, mint, cubebs, thyme, &c.

Experiment proves that of all the above-named substances, those only which may be considered as hydrurets or aldehydes possess the property of uniting with the alkaline sulphites to form definite, crystalline compounds. This character may therefore be added to those assigned by chemists to the hydrurets and aldehydes.

Furfurole, methylic alcohol, the carburets of crude pyroligneous spirit, creosote, benzine, cumene, all the bodies of the class of alcohols and compound æthers, chloroform, sulphuret of carbon, &c., are destitute of action upon the alkaline sulphites.

With respect to ordinary aldehyde, I may remark that the compound of aldehydate of ammonia and sulphurous acid, obtained by Redtenbacher, and isomeric with taurine, enters into the class of compounds treated of in this memoir.

The formation of the compounds in question may be made use of to separate aldehydes in a pure state from hydrocarbons, or other products with which they may be mixed. All that is necessary is to employ cold solutions of alkaline bisulphites of 27°–30° B., and to shake them with the hydrurets; the compound usually crystal-

lizes immediately. Sometimes it is necessary to apply a gentle heat, and prolong the contact some time in closed tubes.

The crystals are collected and purified by crystallization from alcohol. They are very soluble in water.

These compounds generally regenerate the essential oil when they are boiled; in the cold, alkalies produce an analogous decomposition. In general they are very unstable.

In the following table I have summed up the constitution of the compounds which I have analysed; this constitution is represented under two different points of view:—

First hypothesis.	Second hypothesis.
Compound of hydruret of benzoyle—	
$NaO, S^2O^4, C^{14}H^6O^2, 2Aq$	$NaO, C^{14}H^5S^2O^5+3Aq$
Compounds of nitrated hydruret of benzoyle—	
$NH^4O, S^2O^4, C^{14}H^5NO^6+2Aq$	$NH^4O, C^{14}H^4NS^2O^9, 3Aq$
$NaO, S^2O^4, C^{14}H^5NO^6+11Aq$	$NaO, C^{14}H^4NS^2O^9, 12Aq$
Compound of hydruret of salicyle—	
$KO, S^2O^4, C^{11}H^6O^4+Aq$	$KO, C^{14}H^5S^2O^7, 2Aq$
Compound of hydruret of anisyle—	
$NaO, S^2O^4, C^{16}H^8O^4+Aq$	$NaO, C^{16}H^7S^2O^7, 2Aq$
Compound of hydruret of cuminyle—	
$NaO, S^2O^4, C^{20}H^{12}O^2+3Aq$	$NaO, C^{20}H^{11}S^2O^5, 4Aq$
Compound of œnanthylic aldehyde—	
$NaO, S^2O^4, C^{14}H^{14}O^2+3Aq$	$NaO, C^{14}H^{13}S^2O^5, 4Aq$
Compound of capric aldehyde (oil of rue)—	
$NH^4O, S^2O^4, C^{20}H^{20}O^2+3Aq$	$NH^4O, C^{20}H^{19}S^2O^5, 4Aq.$

The ease with which these salts are decomposed by heat has prevented me from coming to any decided opinion as to the most rational hypothesis to be adopted for their constitution. I may observe, however, that the compounds of this class obtained by Redtenbacher and Tilley, by the action of bisulphite of ammonia upon the common and œnanthylic aldehydes, which are anhydrous, agree better with the second hypothesis than with the first.

The constitution of the anhydrous isatosulphite of potash, according to the last experiments of M. Laurent, would support the rational formula $C^{16}H^4NS^2O^7, KO$. Consequently the isatosulphites would appear to belong to the class of compounds which form the subject of this memoir.—*Comptes Rendus*, Nov. 29, 1852, p. 801.

On the Conditions under which Fresh Bread becomes transformed into Stale. *By* M. Boussingault.

It is generally supposed that fresh bread passes by loss of water into the state in which it is termed *stale*. The author shows that fresh bread also goes over into this state when it is kept in a damp place, such as a cellar, and that the hardest and most brittle crust becomes tough and flexible, in order to prove how improbable it is

that the change in the bread depends upon a loss of water. Every one knows also that slices of bread toasted upon a hot plate over the open fire, although they may be heated to carbonization externally, always retain the characters of fresh bread internally.

The author took a loaf of 33 centims. diameter and 14 centims. in thickness, and at the moment of its being taken from the oven inserted into its middle a thermometer, which reached 7 centims. into its substance. In a few moments it was taken out, and showed a temperature of 207° F. That the temperature remained under 212° is readily understood; for even if the oven gave a heat of 482°–572° F., the mass within the crust cannot exceed 212° F., because water evaporates from it. The hot loaf weighed 3·760 kilogrms. It was hung up in a room where the thermometer stood at 66° F.:—

Date.	Hour.	Temperature of the bread.	Temperature of the room.	Weight of the bread in kilogrammes.
June 12.—	9 A.M.	206·6 F.	66·2 F.	3·760
	10	177·8	66·4	
	11	154·4	66·2	
	noon	136·6	66·3	
	1 P.M.	122·4	66·2	3·735
	2	111·2	66·2	
	3	101·5	66·0	
	4	94·5	66·2	
	5	88·9	65·7	
	6	84·0	65·5	
	8	77·0	65·1	
	10	73·4	64·9	
June 13.—	7 A.M.	65·8	64·6	
	9	64·9	64·6	3·730
	10	64·6	64·6	
	11	64·4	64·4	
	noon	64·4	64·2	
	2 P.M.	64·4	64·4	
	7	64·0	63·9	
June 14.—	9 A.M.	62·6	63·3	3·727
June 15.—	9 A.M.	61·0	61·7	3·712
June 16.—	9 A.M.	60·4	61·3	3·700
June 17.—	9 A.M.	..	..	3·696
June 18.—	9 A.M.	..	..	3·690

Near this loaf with the thermometer a second was laid, so as to enable the changes in its substance to be observed. It was shown now, by the observation of the two loaves, that the temperature ceased to change in twenty-four hours, and after the lapse of this time was the same as that of the room. The loaf was now, as usual, half stale, the crust no longer hard. At the same time the entire loss of water amounted to 30 grms., or 0·008 per cent. on the whole weight. On the sixth day the loaf was perfectly stale; the loss by drying now reached 0·01 per cent. According to this it is impossible

that the loss of water is the cause of the well-known change in the bread.

The loaf, which now after six days' drying weighed 3·690 kilogrms., was again put into the oven. The thermometer stood in the middle of the crumb at 158° F. When the loaf was cut up, it was as fresh as at first, and weighed only 3·570 kilogrms. It had thus during refreshing lost 120 grms., or $3\frac{1}{4}$ per cent. of water.

The investigation was now carried on in another way. A slice of hot bread was laid in a dish under a bell-glass, the mouth of which was closed with water, so that the air in the bell-glass was consequently always saturated with watery vapour. The piece of bread was weighed daily at the same hour:—

Weight of the slice of bread	32·05 grms.	Fresh bread.
Weight after 24 hours.....	31·81	Half stale.
Weight after 48 hours.....	31·75	Stale.
Weight after 72 hours.....	31·70	Stale.
Weight after 96 hours.....	31·69	Very stale.

From this, the bread became half stale through a loss of water of 0·007 per cent., and the change of the bread proceeded with a further loss of 0·002, 0·0016, 0·0003 on the original weight.

The slice of stale bread was now toasted. It then weighed 28·65 grms., whilst more than nine-tenths of it was restored to the state of fresh bread.

In a tin-plate cylinder closed with a stopper, the author completely restored stale bread to the fresh state in the course of an hour, by a temperature of 122°–140° F. produced by the water-bath.

The staleness of bread results therefore from a change in its molecular condition, and not from a loss of water.—*Comptes Rendus*, p. 588.

On new Compounds of Tellurœthyle. *By* Prof. Wöhler.

The property possessed by tellurœthyle of behaving like an organic radical or metal, led to the idea of preparing a tellurœthylamine with it. This idea was not confirmed by the experiments undertaken with that object; these, however, led to the discovery of the following compounds, which may be considered as further arguments in favour of the existence of that property. There is now every prospect of these relations being thoroughly investigated, as A. Löwe of Vienna, to whom the author was indebted for the material employed in this investigation, has discovered an advantageous process, by which tellurium, which has hitherto been so rare, may be obtained as a subsidiary product of the working of the gold ore of Transylvania, and brought into the market by the pound.

1. *Oxychloride of Tellurœthyle*, $C^4 H^5 TeO + C^4 H^5 TeCl$.—This substance is produced when the chloride of tellurœthyle is dissolved in caustic ammonia or potash, and evaporated to crystallization. It is better to employ ammonia, as an excess of it does not decompose the product. The salt crystallizes very readily as the

excess of ammonia evaporates. The mother-liquor contains chloride of ammonium or potassium.

It forms very shining, colourless, six-sided prisms. It is decomposed by heat, with evolution of tellurœthyle, leaving a residue of metallic tellurium. It is obtained in particularly beautiful crystals from its solution in hot alcohol.

Muriatic acid added to its solution throws down colourless oleaginous chloride of tellurœthyle, and only a small quantity of this and the excess of the acid remain in the fluid.

Sulphuric acid also throws down chloride of tellurœthyle from the solution; but there remains some sulphate of tellurœthyle dissolved in the fluid, from which muriatic acid still throws down chloride of tellurœthyle. Sulphurous acid throws down a heavy, dark yellow, clear oil, which is a mixture of telluric æthyle and its chloride. From these actions and its mode of production, the composition of this body might be foreseen. It was proved by analysis, which gave—

Carbon	19·94	8	20·89
Hydrogen	4·96	10	4·35
Tellurium	56·22	2	55·87
Chlorine	15·49	1	15·43
Oxygen	3·39	1	3·43

It follows therefore that from 2 atoms of chloride of tellurœthyle the half of the chlorine is abstracted by the alkali and exchanged for oxygen.

2. *Bromide of Tellurœthyle,* $C^4 H^5 TeBr$.—This is produced by adding hydrobromic acid to the solution of the above chlorine compound, or to that of the nitrate of the oxide of tellurœthyle. It is separated in the form of a pale yellow, inodorous, heavy oil.

3. *Oxybromide of Tellurœthyle,* $C^4 H^5 TeO + C^4 H^5 TeBr$.—This is obtained by the solution of bromide of tellurœthyle in ammonia. It crystallizes in shining colourless prisms, of the same form as those of the corresponding chlorine compound, to which it is exactly analogous in its behaviour.

4. *Iodide of Tellurœthyle,* $C^4 H^5 TeI$.—This is formed when a solution of the nitrate of tellurœthyle, or of its oxychloride or oxybromide, is mixed with hydriodic acid. It is also produced instantaneously when this acid is poured over free chloride of tellurœthyle, which explains why the result of the decomposition of the oxychloride is not a compound of the chloride and iodide, but only the latter. It separates in the form of a beautiful orange-yellow precipitate.

After washing and drying, it forms an orange-yellow powder. Heated in water, it fuses at 122° F. into a heavy reddish-yellow liquid. On cooling, it forms a yellowish-red opake mass of large laminar crystals, which is readily divisible. In hot alcohol it forms a reddish-yellow solution, on cooling from which it crystallizes in long, thin, orange-yellow prisms. It is but sparingly soluble in water. When heated beyond its melting-point, it is decomposed,

furnishing a yellowish-red oil, a black sublimate and a residuum of metallic tellurium.

If hydriodic acid which has become brown be employed in its preparation, a nearly blood-red precipitate is produced, which no doubt contains a higher iodine compound.

5. *Oxyiodide of Tellurœthyle*, $C^4 H^5 TeO + C^4 H^5 TeI$.—This is obtained by the solution of the iodide of tellurœthyle in ammonia and spontaneous evaporation. It crystallizes in proportion to the evaporation of the excess of ammonia, being very readily soluble in this liquid, but only sparingly in water. It forms pale yellow transparent prisms, isomorphous with the analogous chlorine and bromine compounds. Exposed to the air, the surface becomes orange-yellow. From its solution in water, muriatic acid throws down a heavy reddish-yellow fluid,—a mixture of chloride and iodide of tellurœthyle. Sulphuric acid throws down orange-yellow iodide of tellurœthyle, from the fluid filtered from which muriatic acid still throws down colourless chloride of tellurœthyle. Sulphurous acid precipitates from its solution a mixture of tellurœthyle and its iodide, which is very fusible, and only becomes semi-solid when cold.

The analysis of this compound was considered superfluous, as its composition may be deduced with security from its behaviour and origin.

No compound could be produced with cyanogen.

6. *Hydrofluoric Acid* precipitates chloride of tellurœthyle from the solution of the oxychloride, and there remains in solution a fluorine compound, which is procurable in the crystalline state by evaporation; it is the same that is obtained from hydrofluoric acid and free oxide of tellurœthyle, a behaviour in which fluorine differs remarkably from the other halogens.

7. *Sulphate of the Oxide of Tellurœthyle*, $C^4 H^5 TeO\,HO + C^4 H^5 TeO\,SO^3$.—This compound was obtained by dropping a hot saturated solution of neutral sulphate of silver into a solution of crystallized oxychloride as long as any chloride of silver was precipitated. The new salt crystallized in groups of small, short, colourless prisms. It is readily soluble in water. Sulphurous acid added to its solution throws down a yellow oleaginous substance of a disagreeable odour. Chloride of barium precipitates sulphate of baryta, and reproduces the oxychloride. The amount of sulphuric acid ascertained to be contained in it was 15·10 per cent.; calculated by the above formula, it should be 15·91 per cent.

8. *Oxalate of the Oxide of Tellurœthyle*, $C^4 H^5 TeO\,HO + C^4 H^5 TeO\,C^2 O^3$, obtained by the digestion of a hot saturated solution of the oxychloride with an excess of oxalate of silver, crystallizes in small groups of short colourless prisms. It is soluble in water with difficulty. By heat it fuses, boils, evolves much tellurœthyle and a crystalline sublimate, and leaves a residuum of metallic tellurium. The quantity of oxalic acid ascertained to be contained in it was 14·86 per cent., that of tellurium 51·31 per cent. The calculated numbers are 14·56 and 51·87.

Hence, therefore, these two salts, which moreover have an acid reaction, are to be considered as double salts, consisting of the neutral sulphate or oxalate combined with the hydrated oxide of tellurœthyle.

Whether the base contained therein be identical with that obtained in the investigations undertaken by Mallet* at the author's request, by the immediate oxidation of tellurœthyle with nitric acid, or by the decomposition of the chloride of tellurœthyle by oxide of silver, or whether it be different from this and possess double its atomic weight (when the composition of the salt must be expressed by $C^8 H^{10} Te^2 O^3 + HO\,SO^3$), the author leaves undetermined.

9. *Oxide of Tellurœthyle.*—As regards the isolation of the base, it appears not to be possible without partial decomposition. It was attempted in two ways, namely, by the decomposition of the oxychloride by means of freshly-precipitated oxide of silver, and by the decomposition of the sulphate by hydrate of baryta. In both cases a solution of hydrated oxide of tellurœthyle, possessing an alkaline reaction and free from baryta or oxide of silver, was obtained; this, however, always smelt like tellurœthyle whilst being evaporated on the water-bath, and at length left behind a mass of the consistence of turpentine, which did not become solid, and in which at this degree of concentration a foaming evolution of gas suddenly took place, as though a carbonic acid salt had been formed and became again decomposed under these circumstances. At first also the mass evolved carbonic acid gas with acids, but not after some time. It no longer formed a clear solution in water. It evolved ammonia from muriate of ammonia. Muriatic acid threw down from its solution chloride of tellurœthyle. Oxide of tellurœthyle appears to be insoluble in very concentrated solution of potash; for if the crystallized oxychloride be heated therewith, colourless oleaginous drops with the odour of tellurœthyle are separated, which again become dissolved on the admixture of water.

The author concludes by remarking, that it may be foreseen that all these reactions will occur with methyle and the other alcoholic radicals, and describes, in consideration of the great promises of important results held out by this subject, the mode of preparation of telluret of potassium, of tellurœthyle and its chloride, for which however we must refer to his memoir.—*Nachr. von der Gesellschaft der Wiss. zu Gött.*, 1852, p. 165.

On Anhydrous Valerianic Acid. By L. Chiozza.

The experiments which I have the honour to submit to the Academy have been undertaken at the suggestion of M. Gerhardt, and form a continuation of those communicated by that chemist. Their object is to bring fresh proofs in favour of the opinion expressed by M. Gerhardt as to the constitution of the monobasic acids, and as to the relations existing between these and their corresponding anhydrous acids. The examination of the homologues of formic acid being

* Chem. Gaz., vol. x. p. 17.

undoubtedly of the most importance in this point of view, and the first terms of this series (the anhydrous acetic and butyric acids) having already been obtained by M. Gerhardt, I have directed my attention to valerianic acid.

The potassic salt of this acid is the best suited for these experiments; it is obtained perfectly pure by evaporating its alcoholic solution to dryness, and heating the residue until it begins to melt.

The valerianate of potash, prepared in this manner, being brought into contact with oxychloride of phosphorus, in the proportion of 6 equivs. of the salt to 1 equiv. of the oxychloride, a very violent reaction immediately takes place; the unbearable odour of the oxychloride of phosphorus disappears entirely, and the mixture becomes transformed into a saline mass impregnated with a thick oily fluid, which only possesses a very feeble odour.

This last substance is *anhydrous valerianic acid.* To obtain it in a pure state, it is sufficient to treat it first with a very dilute solution of carbonate of potash, then with æther, and lastly to evaporate the ætherial solution on the water-bath after it has been shaken with chloride of calcium. The product thus purified having been analysed, furnished numbers agreeing with the formula $C^{10}H^{18}O^3$.

The anhydrous valerianic acid is a limpid oil, possessing considerable mobility and lighter than water. When recently prepared, it has an odour of apples, which is not disagreeable; but when rubbed upon the hands, it communicates to them an odour of valerianic acid, which lasts during several days. Its vapour irritates the eyes, and provokes coughing. Boiling water only changes it very slowly into valerianic acid, whilst this transformation is very rapidly effected by alkaline solutions, and instantaneously by potash in a state of fusion. It boils constantly at about 419° F., and distils in the form of a limpid liquid like water.

The reaction, which produces anhydrous valerianic acid, may be easily understood in the following manner:—The oxychloride of phosphorus, in reacting upon the valerianate of potash, transforms a portion of this salt into phosphate of potash and chloride of valeryle, as shown in the following equation:—

$$3\left(\left.\begin{matrix}C^5H^9O\\K\end{matrix}\right\}O\right)+PCl^3O=PK^3O^4+3\left(\begin{matrix}C^5H^9O\\Cl\end{matrix}\right).$$

Chloride of valeryle.

But the chloride of valeryle acts in its turn upon the valerianate of potash, so that the final product of the reaction consists of phosphate of potash, chloride of potassium and anhydrous valerianic acid. The following equation applies to the second period of the reaction:—

$$3\left(\begin{matrix}C^5H^9O\\Cl\end{matrix}\right)+3\left(\left.\begin{matrix}C^5H^9O\\K\end{matrix}\right\}O\right)=3ClK+3\left(\left.\begin{matrix}C^5H^9O\\C^5H^9O\end{matrix}\right\}O\right).$$

Anhydrous valerianic acid.

The exactness of this mode of interpreting the action of the oxychloride of phosphorus on the salts of the monobasic acids has been placed beyond doubt by the experiments of M. Gerhardt on acetic and butyric acids; it furnishes ground also for predicting that by

this process the anhydrous acids corresponding to the superior homologues of valerianic acid will be obtained, such as the caproic, caprylic, pelargonic, and other acids.

In order to multiply the proofs of the double existence of the group *valeryle* in anhydrous valerianic acid, I prepared an anhydrous acid containing two different groups. By causing chloride of benzoyle to react upon the valerianate of potash, valerianate of benzoyle, $\left.\begin{matrix} C^5 H^9 O \\ C^7 H^5 O \end{matrix}\right\} O$, is very readily obtained.

It is an oil of greater weight than water, which is neutral towards test-papers, and the odour of which is nearly identical with that of anhydrous valerianic acid. Its vapour is acid, and causes a flow of tears. Alkaline solutions transform it into valerianate and benzoate. Submitted to analysis, it gave the numbers required by theory.

The valerianate of benzoyle splits by distillation into anhydrous benzoic and valerianic acids. Nevertheless this separation is not so distinctly effected as in the case of the acetate of benzoyle, and it is necessary to rectify the product several times before obtaining anhydrous valerianic acid in a state of purity.

The property possessed by the anhydrous acids of becoming converted into amides and anilides, when they are made to act upon ammonia or aniline, has enabled me to obtain with anhydrous valerianic acid a new substance, *valeranilide*, which crystallizes in magnificent, elongated, rectangular lamellæ, which are very brilliant and fusible at 239° F.

This substance is formed as soon as anhydrous valerianic acid is brought into contact with aniline. It is not very soluble in boiling water, in which it fuses into clear globules. At a temperature above 428° F., it distils over, in great part, without decomposition. Alcohol and æther dissolve it with facility.

A concentrated boiling solution of caustic potash only attacks it with extreme difficulty, and it is necessary to have recourse to potash in a state of fusion to produce an appreciable disengagement of aniline.

Its crystallization presents a remarkable circumstance, which has already been observed by M. Gerhardt in that of formanilide. It is this, that when valeranilide separates from its solution in diluted boiling alcohol, it sometimes occurs that it takes the form of oily drops scattered through the fluid; it may be kept for several hours in this state, even after the complete cooling of the liquid; but it is only necessary to agitate the vessel slightly to cause the whole mass to become almost instantaneously a jelly of fine needles.

The analysis of valeranilide furnished numbers which agree exactly with the formula $C^{11} H^{15} NO$, which theory assigns to this substance.

I propose to continue these researches upon other acids homologous with valerianic acid, especially with the view of ascertaining the relations that may exist between the points of ebullition of these acids and those of the corresponding anhydrous acids.—*Comptes Rendus*, Oct. 16, 1852, p. 568.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Process for determining the Value of Soap. By Dr. BOLLEY.

To determine the value of a specimen of soap, it is necessary to ascertain,—1st, the per-centage of dry substance; 2nd, the relative proportion of fatty acid and alkali; 3rd, the kind of alkali and fatty acid, or the substance replacing the latter; 4th, the intentional or accidental admixture of foreign organic or inorganic substances.

In most instances the consumer merely determines the per-centage of water in soap, because this is the most usual and almost unavoidable admixture, and one which, as is known, may be present in a soap in considerable quantity, without in an equal degree influencing the exterior appearance, hardness, &c. The means of determining the per-centage of dry substance are,—1st, drying a weighed quantity in a water-bath; and 2nd, salting out, or introducing the soap into a saturated solution of chloride of sodium and boiling, by which means it concretes together into a solid mass tolerably free from water. With regard to the first method, many have no doubt found that when the soap has been heated for a long time in a water-bath, and has commenced to melt, it not only does not give off any more water, but becomes very hygroscopic, and attracts moisture again very rapidly.

Old Marseilles soap, exposed to a temperature of 86° F. for six hours, was found to have lost 3·2 per cent., and when kept at 212° F. for two hours, there was no further diminution in weight; after exposure to the air for a few hours, it weighed 1 per cent. more than at first. Several other specimens showed that soap, when heated to 212° F., increased in weight during the weighing. If such experiments were carried out by inexperienced persons, errors would be the natural consequence. The process of salting out may be applicable upon a somewhat large scale, with for example a pound of soap, and is then better adapted than the other to give trustworthy indications of the per-centage of actual soap. But the determination of dry soap has no bearing upon the very important question of the possible presence of adulterating substances, still less upon the second and third points mentioned above.

It is by no means difficult to determine the quantity of alkali and that of fat in a soap; but the operation is far more tedious and troublesome when it is at the same time requisite to ascertain whether the soap contains free alkali or fat, and the proportion of one or other to the fat and alkali in combination. Nevertheless this question may not generally be of great consequence, as both errors would scarcely be owing to a fraudulent intention, and their magnitude would be confined within a narrow limit. The uncombined alkali in hard (soda) soap may be determined by exposing the soap in fine shavings to the air, so that the alkali may absorb carbonic acid, treating it with strong alcohol, and examining the insoluble residue, which may contain other salts or insoluble substances, for

alkali. A process recommended by Stöckhardt is less troublesome; it consists in adding to a hot concentrated solution of soap, bitartrate of potash until the fatty acids begin to separate. The larger the quantity of bitartrate requisite, the larger the quantity of free alkali. This is certainly a mere comparative test, applicable to the examination of a number of different specimens of soap. It is not improbable that unsaponified fat is sometimes present in soap. Dumas determines it by separating all the fat by means of hydrochloric acid, re-saponifying with baryta-water, and extracting the baryta-soap with alcohol, which dissolves only the unsaponified fat.

The process now to be described does not take into consideration the quantity of free and combined fat or alkali, but includes the estimation of all the four above-named conditions which determine the value of a soap, and is at the same time serviceable and easily carried out.

A gramme of the soap is weighed; hard soap in shavings; soft soap is weighed to *near* a gramme, because the addition and abstraction of small quantities is more inconvenient than a reduction in the calculation. The soap is introduced into a beaker-glass holding about an ounce, treated with a small quantity of æther, in which it does not dissolve, and then with a rather smaller volume of pure acetic acid; two layers are thus formed; the soap is rapidly dissolved; the upper layer containing the æther and fat or resin, with a little acetic acid; the lower layer, water, alkali combined with acetic acid, free acetic acid, the salts usually formed in the manufacture of soap, chloride of sodium, alkaline sulphate, and finally the foreign admixtures, whether soluble in water or not. If sand, powdered pumice-stone, clay, steatite, heavy spar, &c., are present, they remain at the bottom of the glass. Other substances of organic origin, such as starch, &c., are suspended in the layer of liquid beneath the æther. The entire mass is then poured off from the undissolved substances in the beaker into a large pipette, widened in the middle and bent upwards at the lower extremity so as to form a kind of separator. The liquids are allowed to remain in the wide part of the pipette until they have perfectly separated into two layers, and it may then be so managed that none of the ætherial liquid enters its lower extremity, which is turned upwards. The beaker-glass, together with the residue, if any, is then washed with æther and water, which are poured into the pipette; and by inclining it, or blowing gently into the upper end, the liquids may be partially separated. The addition of successive quantities of distilled water will then wash the ætherial liquid perfectly free from saline matters. This being effected, the ætherial solution of fat, together with the small quantity of water beneath it, are poured back into the empty beaker-glass, and the pipette is washed out with a mixture of strong alcohol and æther. A great advantage is thus gained, inasmuch as the small layer of water beneath the æther is rendered miscible with it by means of the alcohol; and if this is not the case at first, a few drops of alcohol must be added. It is for this reason advisable to avoid introducing too much water into the mixture when washing

out the contents of the pipette into the beaker. It is also convenient to have the weight of the beaker marked upon it with a diamond. The ætherial liquid is then placed upon a water-bath, and left until nothing remains but the fat or resin, which, without altering the general principle of the process, may readily be recognised. When a trace of aqueous liquid remains beneath the fat, it is very difficult to remove it by evaporation, and the addition of alcohol to the æther is a very appropriate means of obviating this difficulty. When the smell of æther, alcohol, and acetic acid has become very feeble, the residue is weighed, and the weighing repeated after a longer-continued application of heat; it rarely happens that any decrease of weight is perceived on the second weighing, when the evaporation is carried far enough in the first instance. When several experiments are made successively with the same soap, the per-centage of fat comes out in the several determinations agreeing in the second decimal place.

The fatty acid from 1 grm. of soap forms a layer of such thickness, that by slightly inclining the beaker-glass, the bulb of a small thermometer can be introduced, so as to determine the melting-point, by which means some idea may be formed of the kind of fat. If any insoluble residue remains in the beaker after the first treatment of the soap, it is dried and weighed, and its nature determined. The aqueous liquid which is separated from the ætherial solution of fat is introduced into a small capsule*, and carefully evaporated to dryness in a water-bath. The residue is weighed, and ought not to suffer any further diminution of weight when again heated in the bath. The presence of gelatine may be detected during evaporation by the appearance, starch by means of iodine solution, cheese-curd by the peculiar empyreumatic odour evolved on the application of a sufficient heat; other substances may likewise be readily detected. Their total quantity is estimated by the loss of weight on ignition. If the perfect clearness of the aqueous liquid, the small residue left on evaporation, and its radiated crystalline appearance, indicate that saline substances only are present, the residue may be ignited at once and a previous weighing dispensed with. In this case the ash should contain very little carbon, and after this has been perfectly burnt off, it may be examined to determine the quantity and kind of mineral substances it contains. Silica, if it has been added in the gelatinous form, will have become insoluble, and may be separated by filtration and weighed. The filtrate must be examined for sulphate of potash and chloride of sodium, and their quantity determined when there is reason to suppose that they are greater than could be accounted for merely by the impurity of the alkali used in the manufacture of the soap, or the introduction of chloride of sodium during the process. In case it is unnecessary to determine the admixtures named, the total per-centage of alkali may be ascertained by treating the ignited residue with hydrochloric acid, evaporating to dryness, weighing, and calculating from the chloride of

* A platinum or silver capsule, two inches in diameter, with a cover, so that it can be used as an evaporating dish or crucible, is the most convenient.

potassium or sodium the quantity of soda or potash. When it is necessary to ascertain whether besides soda there is potash present, or the reverse, this must be done according to the general rules of analysis, which it is not necessary to particularize here. The same remark applies to several other points. My object in the present instance is to furnish the chemist with a short method of ascertaining the value of soap, leaving the detailed execution of it to his own management.

For the usual purpose, then, this method enables us to determine the per-centage of fat* and its melting-point, the insoluble admixtures,—sand, heavy spar, pumice-stone, &c. The loss on ignition gives approximatively the organic admixtures. The saline residue, converted into chlorine compounds, indicates the per-centage of alkalies; in that from soda soaps, 58 parts are equal to 31 soda; and in potash soaps, 74 chloride of potassium are equal to 47 potash. The sum of these constituents (in centigrammes) deducted from 100 gives the per-centage of water.

On the Analysis of Oils by means of Sulphuric Acid.
By M. Maumené.

Fatty oils, when mixed with sulphuric acid, evolve heat. This property may serve to distinguish them: it distinctly separates the drying oils from those which are not so.

50 grms. of olive-oil were placed in an ordinary test-glass. The temperature having been ascertained by a thermometer immersed in the fluid, 10 cub. centims. of boiled sulphuric acid (1·834 sp. gr.) were *carefully* poured into it. The liquids were then mixed by stirring them with the thermometer, the rising of the mercury being watched at the same time. Commencing with a temperature of 77° F. for the oil and acid, the thermometer rose to 153° F.; increase 76° F. The mixture does not take more than two minutes. The maximum temperature is attained in one.

In another glass of the same kind, 50 grms. of poppy-oil were placed, and similarly treated with acid. From 79° F. the thermometer rose to 213° F.; increase 134° F.

It is necessary to observe, in this case,—1st, a very distinct evolution of sulphurous acid, which is not produced with olive-oil; 2nd, a considerable puffing up of the fluid. In consequence of these two circumstances, the number 134° is too low. The difference between 76° and 134° is sufficient to afford a means of analysis. The experiment, repeated several times under the same conditions with the same olive-oil, has constantly given the same elevation of 76° F.

Experiments made upon olive-oil from different sources proved

* The per-centage of fat comes out somewhat higher than it really is, since the fatty acids are separated in the hydrated state, while in combination with potash and soda they are anhydrous. This circumstance is generally overlooked in the examination of soap, because the high equivalents of the fatty acids render its influence slight.

that the action of sulphuric acid is constant when the oil is pure and when the operation takes place at the same temperature.

The action of the acid is not less constant upon the poppy oil. Experiments showed also that the actual amount of heat developed by this oil is 160° F., instead of from 128° to 134° F., as indicated by the above experiment.

This process of analysis may be applied to the olive-oils of commerce. These oils are frequently only adulterated with poppy-oil, and in this case their analysis may be exactly performed, if their qualitative composition be first ascertained.

But what would take place in case of adulteration with other oils? In order to reply to this question, I have determined the elevation of temperature produced by most of the pure oils. The result of my researches is, that oil of ben and oil of suet evolve pretty nearly the same amount of heat as olive-oil;

That the other oils produce a more considerable elevation of temperature, by means of which they may readily be distinguished from olive-oil; lastly,

That drying oils give much more heat than those which do not possess that property, and may be readily recognised thereby.

Oil of ben and oil of suet cannot be mixed with olive-oil; consequently whenever the latter gives an increase of temperature of more than 76° F., on its mixture with 10 cub. centims. of boiled sulphuric acid (at a temperature of 77° F.), it is not pure.

The preceding statement appears to me sufficient to show the use that may be made of sulphuric acid in the analysis of oils. In mixtures consisting only of two oils, the employment of this acid will assist greatly in determining the quality. Qualitative analysis having been effected, the quantities may frequently be thus deduced with precision.—*Comptes Rendus*, Oct. 16, 1852, p. 572.

PATENT.

Patent granted to T. Skinner, *for Improvements in producing Ornamental Surfaces on Metal, Ivory or Bone.*

This invention relates, first, to certain means of producing ornamental surfaces on metal; and, secondly, to certain means of ornamenting ivory and bone.

The first part of the invention consists chiefly in the use of the combined processes of transferring impressions from engraved or printed surfaces on to metal, and electro-plating or electro-gilding them after biting out the metal, so as to leave the design either sunken or in relief. The metal surface to be ornamented is first well cleansed, which may be effected by rubbing with wash-leather and powdered lime. An impression, taken by preference on tissue-paper, is placed face downwards on the clean metal surface, and rubbed on the back with flannel or other suitable material, so as to transfer it to the metal surface; and when this has been done, the

paper is washed or sponged off; if stronger paper is used for taking the impressions, the back of the paper is smeared over with black lead, and rubbed with a smooth ivory or other hard surface; after which the paper may be stripped off from the metal. A ground or coating of dissolved gum (by preference gum guaiacum dissolved in spirits of wine) is laid with a camel's hair brush over the metal; and when the ground is dry, the impression is washed off by means of a little cotton or other suitable material; this may readily be done, as the gum does not fix itself to the impression. Those parts of the metal which were previously covered by the impression being thus left clean, are now bitten out with acid in the manner practised by engravers; and after this the ground is removed.

Or, in place of proceeding in the above manner, the process may be reversed, and the acid caused to act upon every part of the metallic surface which is not covered by the impression. For this purpose, when the impression has been obtained on the metal, it is sprinkled over with powdered resin, asphaltum, or other suitable matter, which will adhere to the impression, but not to the clean metal; and after the superfluous powder has been removed, the resinous matter is caused to melt and adhere to the impression by warming the metal. When the impression has been thus protected by a coating that will resist the action of the acid, the other parts of the surface are bitten out, and then the impression is removed by a suitable solvent.

The metal surfaces which have been treated according to either of the above methods, are to be prepared for electro-plating or electro-gilding by removing the effect of the acid; this is done by the use of hot water, in which a small quantity of potash or soda has been dissolved, and by scratching with a wire-brush. The metal surfaces are afterwards electro-plated or electro-gilded by any of the known processes.

Although this part of the invention consists chiefly in ornamenting metallic surfaces by the combined processes above described, the patentee likewise proposes to produce ornamental surfaces on Britannia metal and German silver, by simply transferring impressions and biting them out with acid, without subsequently electro-plating or electro-gilding the same.

The following are the means of ornamenting surfaces of ivory and bone, which form the second head of this invention:—An impression is first transferred on to ivory and bone in the manner above described; then the surface is covered with a coating of gum, and the impression removed with turpentine, as before; after which the pores of the ivory or bone are opened by the application of diluted acid, and by the aid of ink or dye the parts from which the impression has been removed are dyed; or the dyeing may be effected without the application of acid. Or the parts may be bitten out with acid, and the work filled in with sealing-wax, dissolved in spirits of wine, or other suitable solvent. Gum-lac, or other substances, may be used instead of sealing-wax, and the work may be buffed in order to give it a high polish.—Sealed August 14, 1851.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of the Leaves of Arctostaphylus Uva-Ursi.

By A. KAWALIER.

THE leaves of the Arbutus, according to former examinations, contain tannin and a crystalline substance of a bitter taste, which has been called *arbutine*.

If the leaves be treated with boiling water, a brownish-yellow decoction is obtained, which, when mixed with solution of acetate of lead, gives a precipitate of a pale yellow colour with a greenish tinge. The fluid filtered from the lead salt is of a pale wine-yellow colour. It contains some sugar, arbutine, ericoline and a resinous substance.

Gallic Acid.—The precipitate produced in the decoction of arbutus-leaves by solution of neutral acetate of lead was washed with water, formed into a paste, and decomposed by sulphuretted hydrogen gas. The liquid filtered from the sulphuret of lead was evaporated in a stream of carbonic acid gas to the consistence of weak syrup. At the end of twenty-four hours brownish crystals were deposited, which were pressed between blotting-paper, dissolved in boiling water, and treated with animal charcoal. The fluid, filtered hot from the animal charcoal, gave colourless crystals, which were obtained perfectly pure by repeated crystallization. Their watery solution exhibits with salts of peroxide of iron, and with other reagents, the behaviour of a solution of gallic acid. Analysis gave 44·42 per cent. of carbon. Crystallized gallic acid, $C^{14} H^6 O^{10} + 2HO$, requires 44·68 per cent. of carbon.

A hot solution of the acid, precipitated by a hot solution of acetate of lead, gave a lead salt of a white colour with a greenish tinge. This contained 13·76 per cent. of carbon and 72·56 per cent. of oxide of lead. The formula $C^{14} H^6 O^{10} + 4PbO$ requires 13·63 per cent. of carbon and 72·41 per cent. of oxide of lead.

As the decoction of the leaves was made in a closed distillatory apparatus, the washing of the lead salt by decantation effected in a close vessel, and as the fluid obtained by the decomposition of the latter with sulphuretted hydrogen was evaporated in a stream of carbonic acid gas and allowed to cool *in vacuo*, the gallic acid cannot result from the alteration of another substance, such as the tannic acid of galls, but must exist ready formed in the leaves.

Arbutine, $C^{32} H^{24} O^{21}$ (air-dried).—When the pale yellow fluid fil-

tered from the gallate of lead is distilled in a retort, a little more lead salt is separated, which is filtered out. Sulphuretted hydrogen gas is passed into the fluid, which is then filtered from the separated sulphuret of lead. When yeast is then added to the filtrate, fermentation commences in consequence of its containing some sugar, but without any decomposition of the arbutine taking place. If this fluid, whether it has been submitted to fermentation or not, be evaporated to the consistence of syrup and allowed to stand for several days, prisms of arbutine separate in stellate groups. The entire fluid sets at last into a crystalline jelly. This is placed upon fine linen, the mother-liquor allowed to drain off, and the crystals, which are of a faint brown tint, pressed, by which they remain nearly colourless. By solution in boiling water and treatment with animal charcoal, the arbutine is obtained pure in long, acicular, colourless crystals, united in tufts and possessing a bitter taste. It gave the following composition:—

Carbon.....	49·93	32 =	192	50·00
Hydrogen.....	6·32	24	24	6·25
Oxygen.....	43·75	21	168	43·75

The crystals of arbutine are soluble in water, alcohol and æther; fuse at an elevated temperature into a clear colourless fluid, which solidifies on cooling into an amorphous colourless mass, in which many fissures are formed. At 212° F. the crystals undergo no apparent change. Solutions of arbutine do not act on vegetable colours; salts of peroxide of iron, solutions of neutral and basic acetate of lead, produce no precipitate in its aqueous solution. Dried at 212° F., the air-dried crystals of arbutine lose water, but not their transparency. Analysis gave:—

Carbon.....	52·44	52·42	32 =	192	52·46
Hydrogen	6·16	6·06	22	22	6·01
Oxygen	41·40	41·52	19	152	41·53

From these analyses it follows that air-dried arbutine loses 2 equivs. of water at 212° F.; $C^{32}H^{24}O^{21}=C^{32}H^{22}O^{19}+2HO$. It loses no more on fusion.

Arbutine dissolved in water was left for several days in a closed vessel in a moderately-warm place in contact with emulsine, prepared by triturating sweet almonds with water, adding acetic acid, filtering, and precipitating the filtrate with alcohol. The colourless fluid acquired a red colour, became warm, smelt slightly like carbolic acid, and no longer had a pure bitter taste like the original solution of arbutine. On evaporation on the water-bath, there remained a solid brownish-yellow residue, which was powdered and extracted with æther. The portion insoluble in æther was dissolved in boiling water, and the solution treated with animal charcoal and evaporated. Crystals were formed after long standing, and at last the entire mass changed into crystals of grape-sugar. This grape-sugar was dried both at a temperature of 212° F. and at the ordinary temperature *in vacuo* over sulphuric acid. Both these were submitted to analysis, when the latter gave—

Carbon	36·64	12 =	72	36·36
Hydrogen	7·05	14	14	7·07
Oxygen	56·31	14	112	56·57

Arctuvine, $C^{32}H^{24}O^{21}$.—The ætherial solution, which left the grape-sugar undissolved, gave on evaporation brown crystals, which were dissolved in water. Animal charcoal was added to the solution, which was filtered after standing on the charcoal twenty-four hours. By gradual evaporation in a cool place, crystals of an inch in length and half an inch in thickness were deposited. The brown colour arises from a small quantity of an impurity, which however amounts to so little, that, as shown by the analysis of the brown crystals, it has no influence upon the result of the analysis.

By repeated crystallizations from water, alcohol or æther, and treatment with animal charcoal, colourless crystals, of 4 or 6 lines in length and 2 or 3 lines in thickness, were obtained. They are four-sided prisms, of a bitter-sweet taste. When heated, they melt; at 212° F. they undergo no change. By careful heating they may be sublimed.

In the following analyses, I. is that of the brown crystals, II. of colourless prisms crystallized from alcohol, and III. of colourless long needles crystallized from alcohol and recrystallized from water.

	I.	II.	III.			
Carbon	64·35	64·55	64·34	20 =	120	64·51
Hydrogen ..	5·65	5·57	5·70	10	10	5·38
Oxygen	30·00	29·88	29·96	7	56	30·11

The formula of arctuvine is therefore $C^{20}H^{10}O^{7}$, and it is the only product formed, with grape-sugar, by the action of emulsine upon arbutine:—

$C^{32}H^{24}O^{21}$, air-dried arbutine, $= C^{20}H^{10}O^{7}$, arctuvine, $+ C^{12}H^{14}O^{14}$.

The addition of basic acetate of lead and a little ammonia to a watery solution of arctuvine produces a white precipitate, which soon becomes discoloured and brownish-gray. If a solution of chloride of iron be added by drops to a watery solution of arctuvine, each drop of the solution of iron produces a blue colour, which in the next instant becomes green and disappears; the solution becomes brownish-yellow. Arctuvine therefore, like saligenine, forms, on the addition of a salt of peroxide of iron, a blue compound, which however disappears because the iron salt oxidizes the arctuvine.

Arctuvine, when brought into contact with a solution of bichromate of potash, becomes oxidized immediately; a brown precipitate is formed, which is redissolved by boiling with an excess of the solution of bichromate of potash, giving a solution of a dark brownish-red colour. Very little separates on cooling. If, however, muriatic acid be added to the filtered solution, the oxide of chrome compound is thrown down in flakes of a blackish-brown colour. Its composition, which however is not constant, agrees best with the formula $2(C^{20}H^{13}O^{25}) + HO + 3Cr^{2}O^{3}$.

If arctuvine, moistened with a little water, be exposed to the ac-

tion of ammoniacal gas with access of air, it speedily acquires a black colour. This nitrogenous compound, dried at 212° F., is gray, but when moistened with water again becomes black. Analysis gave:—

Carbon.....	35·88	20 =	120	36·14
Hydrogen.....	3·03	10	10	2·01
Nitrogen	12·52	3	42	12·65
Oxygen.....	48·57	20	160	48·20

If the formula be written $C^{20}\,H^{10}\,N^{3}\,O^{20} = C^{20}\,H^{6}\,N^{2}\,O^{19} + NH^{4}\,O$, the formation of this substance, to which the author gives the name of *arctuveïne*, from arctuvine, is shown to result from the assimilation of 2 equivs. ammonia and 12 oxygen, and the elimination of 10 equivs. of water, $C^{20}\,H^{10}\,O^{7} + N^{2}\,H^{6} + 12O - 10HO = C^{20}\,H^{6}\,N^{2}\,O^{19}$, which substance combines with 1 equiv. of oxide of ammonium.

From the formula of arctuvine, $C^{22}\,H^{12}\,O^{7}$, it appears that this substance may be considered as a camphor or as an oxide of an oil, $C^{10}\,H^{8}$, in which a portion of the hydrogen is displaced by oxygen, $C^{40}\,H^{20}\,O^{14}$, 2 equivs. arctuvine, $+ H^{12} - O^{12} = C^{40}\,H^{32}\,O^{2}$, or $2 . (C^{20}\,H^{16}\,O)$.

Oil of turpentine and many other essential oils, the camphor of the Laurineæ, &c., contain carbon and hydrogen in the same proportions, viz. 5 : 4.

Arctuvine also contains the elements of 1 equiv. of oxalic acid and 1 equiv. of salicylite of oxide of æthyle, $C^{2}\,O^{3} + C^{8}\,H^{5}\,O + C^{14}\,H^{5}\,O^{3} = C^{20}\,H^{10}\,O^{7}$. A substance occurs in *Gaultheria procumbens*, which under certain circumstances furnishes salicylate of oxide of methyle. *Gaultheria procumbens* belongs to the same natural family as *Arctostaphylos Uva-Ursi*. Arctuvine is gallic acid from which the elements of oxalic and formic acids have separated,—

$C^{28}\,H^{16}\,O^{24}$, hydrated gallic acid, $= C^{20}\,H^{10}\,O^{7}$, arctuvine, $+ 3(C^{2}\,HO^{4})$, oxalic acid, $+ C^{2}\,H^{2}\,O^{4}$, formic acid, $+ HO$.

From the separation of arbutine into sugar and a neutral substance (arctuvine), it follows that arbutine is a substance nearly allied to salicine and phloridzine. Just like phloridzine, it acquires, by contact with air and ammonia, a blue colour, although extremely faint. Arctuvine may be considered as an oxide of a radical, $C^{10}\,H^{5}$, which might also be regarded as contained in phloretine, if Liebig's formula $C^{30}\,H^{15}\,O^{10}$ be received:—Arctuvine $= 2 . (C^{10}\,H^{5}) + O^{7}$, and phloretine $= 3 . (C^{10}\,H^{5}) + O^{10}$.

A substance is contained in the leaves of the *Arctostaphylos*, which like emulsine possesses the property of causing arbutine to split up into sugar and arctuvine. From a mother-liquor from which arbutine had been crystallized, crystals of arctuvine were obtained after standing several weeks; the presence of arctuvine in the fluid could not previously be detected. All the arbutine can be removed from the mother-liquor by treatment with æther; it then contains, if it has not been set in fermentation by yeast, sugar with ericoline and a brown resinous matter.

Resinous Matter.—If muriatic or sulphuric acid be added to the mother-liquor of arbutine, and the whole be warmed, a resinous mass is separated, which may be purified by solution in alcohol, and precipitation of the filtered solution by water. Dried at 212° F., this substance gives a brittle, nearly black resin, which is easily pulverized, forming a dark brown powder; this, when heated, melts, and when ignited burns with a smoky flame. It furnished on analysis—

Carbon	62·99	62·92	80 =	480	62·90
Hydrogen	5·32	4·80	35	35	4·58
Oxygen	31·69	32·28	31	248	32·52

$C^{80} H^{35} O^{21} = 2(C^{40} H^{17} O^{15}) + HO$. $C^{40} H^{17} O^{15} = C^{40} H^{32} - H^{15} + O^{15}$. Now $C^{40} H^{32}$ is the composition of oil of turpentine, or of a polymeric compound.

Ericinole, $C^{20} H^{16} O^{5}$.—In the mother-liquor of the arbutine there is a substance (ericoline), which is also contained in small quantity in the herb of *Erica vulgaris*, and in the leaves of *Erica herbacea* and of *Rhododendron ferrugineum*, and in larger quantities in the leaves of *Ledum palustre*. The leaves of *Arctostaphylos* also contain a small quantity of this substance, which is decomposed by warming with muriatic or sulphuric acid, and then furnishes a volatile oil. Hence it results, that, in the preparation of the above-mentioned resin a volatile oil evaporates with the water; this is ericinole, which owes its origin to the decomposition of ericoline.

This oil possesses a peculiar and not unpleasant smell; when freshly prepared, it is colourless, but it rapidly attracts oxygen, and then acquires a dark brown colour. According as it has had more or less opportunity of attracting oxygen, it contains more or less of that element; it contains carbon and hydrogen, as shown by the following analysis, in the same proportions as oil of turpentine:—

Carbon	68·15	20 =	120	68·18
Hydrogen	9·37	16	16	9·09
Oxygen.....	22·48	5	40	22·73

Besides the above substances, the leaves of the *Arctostaphylos* contain wax, fat and chlorophylle, vegetable fibre, and traces of a tannic acid, together with gallic acid.—*Sitzungsber. der Akad. der Wiss.*, July 1852.

On the Influence of Water upon Boracic Acid in Borates. *By* H. Rose.

Water behaves towards boracic acid in its salts as it does towards carbonic acid. It is able to expel both acids from their salts, and this frequently takes place more completely in the case of boracic acid than in that of carbonic acid.

I. Atomic proportions of chloride of calcium and of neutral borate of soda, $NaOBO^3 + 8HO$, each salt dissolved in 12 parts of cold water, were mixed. The solution of borax, as it readily attracts carbonic acid, had first been kept boiling for some time, and allowed

to cool in a well-stopped vessel. The precipitate was collected on a filter, and pressed without washing. The filtered fluid contained 1 part of chloride of calcium in solution, forming a soluble compound with the borate of soda, which is decomposed by the addition of more borax.

The precipitate, after pressure, was free from carbonic acid; in drying at 212° F., it attracted some carbonic acid. After calcination, it dissolved in muriatic acid without evolution of carbonic acid. According to Weber's analysis, this precipitate, dried at 212°, has the composition $CaO, BO^3 + 2HO$:—

		Oxygen.		
Lime	31·90	9·07	6	33·22
Boracic acid	40·21	27·65	6	41·20
Carbonic acid	4·42	3·21	1	4·33
Water	20·18	17·94	12	21·25
Chloride of sodium	2·01			
Chloride of calcium	1·28			

The precipitation of the lime-salt by a solution of neutral borate of soda is thus exactly analogous to that produced by the neutral carbonate. In this case also a neutral salt is formed, and in the precipitation water can no more expel boracic acid from the borate of lime than carbonic acid from the carbonate.

When the salt, dried at 212°, was further dried at 392°, it suffered a loss of 10·67 per cent. The salt had then the composition $CaO, BO^3 + HO$. The small quantities of chlorides of calcium and sodium enumerated in the analysis arise from the circumstance, that the salt, as above stated, was not washed:—

		Oxygen.		
Lime	36·43	10·36	5	36·81
Boracic acid	47·98	32·00	5	45·66
Carbonic acid	4·96	3·60	1	5·76
Water	10·63	9·45	5	11·77

The salt was now dried at 572° F. Even at this heat the water is not completely expelled. The salt, dried at this temperature, had the composition $2CaO\ BO^3 + HO$. Analysis gave—

		Oxygen.		
Lime	38·60	10·98	5	39·61
Boracic acid	50·87	34·98	5	49·13
Carbonic acid	5·24	3·81	1	6·20
Water	5·29	3·70	2	5·06

II. The precipitate of the previous investigation was again prepared, and now washed with water; nevertheless it could not be perfectly washed, because the salt dissolved too readily. During the washing and drying the precipitate had attracted carbonic acid. After drying at 212°, the salt has the composition $CaO\ BO^3 + 2HO$, that is to say, no acid is driven out by the water, as the following analysis shows:—

		Oxygen		
Lime	33·00	9·38	5	33·64
Boracic acid.....	40·03	27·53	5	41·73
Carbonic acid	5·09	3·70	1	5·26
Water	19·07	16·95	9	19·37
Chloride of sodium	2·08			
Soda.....	0·73	0·19		

III. Boiling solutions of atomic proportions of chloride of calcium and neutral borate of soda (in 12 parts of water) were mixed, and allowed to boil a few minutes; the precipitate was collected on a filter, and pressed between paper. In this state the precipitate was still free from carbonic acid, which was only attracted during drying. The filtered fluid had a strong alkaline reaction; it was not rendered turbid by solutions of chloride of calcium, or of neutral and common borax, but with oxalic acid it gave a strong precipitate of oxalate of lime; it contained therefore borate of lime, or a soluble double compound of chloride of calcium with borate of soda, and that in such a proportion that it is not decomposed by the addition of the latter. The analysis of the compound, dried at 212°, gave—

		Oxygen.		
Lime	34·86	9·91	11	36·74
Boracic acid	40·51	27·85	10	41·42
Carbonic acid	3·26	2·37	1	2·61
Water.....	19·10	16·98	18	19·23
Soda	0·09	0·02		
Chloride of sodium ..	2·18			

The composition of the precipitate is essentially $CaO\,BO^3 + 2HO$. The neutral borate of lime is however decomposed by hot water, so that the carbonic acid is more intimately united with the lime in the corresponding salt, than the boracic acid in this.

IV. In these experiments the lime was thrown down by common borax. The precipitates produced by the biborate of soda are very different from the bicarbonates. Precipitations by bicarbonate of soda gave simple carbonate of lime. The biborates gave acid salts, but less acid than the borate of soda employed. A part of the boracic acid is expelled by water, but the resulting hydrate of lime unites so intimately with the precipitated biborate of lime, that carbonic acid is not attracted during drying. We have here therefore combinations of a borate with a hydrate, which in consequence of a mutual affinity resist the action of water with great obstinacy, like those with which we are acquainted of carbonates with hydrates, in which this is also the case. These compounds, however, only contain neutral carbonates, whilst acid borates also unite with hydrates, and do not even lose their water at high temperatures.

Equivalents of chloride of calcium and borax were dissolved, each in 12 parts of cold water, and mixed. The solution filtered from the precipitate still contained a soluble compound of chloride of calcium with borate of soda. The precipitate is soluble in water. It was pressed between paper, but not washed. Dried at 212°, it

has essentially the composition $CaO, BO^3+2(CaO+2BO^3)+9$ or $8HO$, or more probably $5(CaO, 2BO^3+3HO)+CaO, HO+HO$. The analyses of the salt, dried at 212°, gave—

		Oxygen.		
Lime	24·70	7·02	3	24·83
Boracic acid	49·80	34·25	5	51·34
Water	22·01	19·56	9	23·83
Soda	1·18	0·30		
Chloride of sodium	2·31			

According to a second investigation, the composition of the substance, dried at 212°, was as follows:—

		Oxygen.		
Lime	25·37	7·21	3	25·51
Boracic acid	50·58	34·79	5	52·73
Water	20·47	18·20	8	21·76
Soda	1·20			
Chloride of sodium	2·38			

The salt, dried at 212°, experienced a further loss of water at higher temperatures, namely,—

10·47 per cent. at a temperature of 392° F.
15·23 per cent. at a temperature of 572° F.
20·47 per cent. at a red heat.

The composition of the substance, calculated from the loss of water at 392° F., is as follows:—

		Oxygen.		
Lime	28·25	8·03	6	29·06
Boracic acid	57·59	39·62	10	60·09
Water	10·10	8·98	7	10·85
Soda	1·30	0·33		
Chloride of sodium	2·76			

The composition, according to the loss at 572°, is—

		Oxygen.		
Lime	29·87	8·49	3	30·48
Boracic acid	59·69	41·05	5	63·02
Water	6·17	5·48	2	6·50
Soda	1·36	0·35		
Chloride of sodium	2·91			

The compositions, corresponding to the losses of water, are—

$5(CaO+2BO^3+3HO)+CaO\ HO+HO$ at 212°.
$5(CaO+2BO^3+\ HO)+CaO\ HO+HO$ at 392°.
$5(CaO+2BO^3+\frac{1}{2}HO)+CaO\ HO$? at 572°.

Thus, by the chemical action of water, a portion of the boracic acid may be expelled from the biborate of lime and replaced by water, and the water of the hydrate of lime of the resulting compound, as is the case with hydrate of lime produced by ordinary means, can only be driven off at a red heat.

The calcined salt is $3CaO+5BO^3$; it is obtained pure by mixing

together cold solutions of borax and chloride of calcium, in such a manner that undecomposed borax may still be present in the filtered solution, and that a precipitate may be formed in it by means of chloride of calcium. The precipitate is washed with water until this produces a yellowish-brown precipitate with a neutral solution of nitrate of silver, and only a very slight degree of opalization becomes perceptible after the addition of nitric acid. The precipitate indeed always contains some chlorine, but in very small quantity.

V. The process is the same as in IV., but the precipitate is to be washed with cold water. The washing cannot be completely effected, because, as has already been stated, the precipitate is soluble. The washing was obliged to be stopped, because only a small quantity of the bulky precipitate remained on the filter. The wash-water becomes at length a nearly pure solution of borate of lime. Like a dilute solution of borax, it produces a brown precipitate of oxide of silver in a solution of nitrate of silver. The composition of the substance, dried at 212° F., is—

		Oxygen.		
Lime	26·88	7·64	2	27·60
Boracic acid	50·06	34·43	3	50·63
Water	21·30	18·93	5	20·77
Soda	1·53	0·39		
Chloride of sodium	0·23			

In this case still more boracic acid has been extracted from the compound by the more protracted action of the water. The substance also contains a little carbonic acid; its composition is $3(CaO, 2BO^3 + 3HO) + CaO\,HO$.

If cold solutions of borax and chloride of calcium are mixed together in such a manner that undecomposed chloride of calcium is still contained in the filtered liquid, and that borax produces a strong precipitate in it, $2CaO + 3BO^3$ is always obtained. If this be washed as completely as possible, it has the composition $3(CaO + 2BO^3 + 3HO) + CaO\,HO$. This does not lose all its water at a temperature of 572° F., but still retains somewhat more than 3 atoms.

VI. Solutions of the same two salts in 12 parts of water were mixed in atomic proportions. The precipitate is very soluble in hot water. It was pressed, without washing, between filtering paper. When dried at 212° F., it had the composition—

		Oxygen.		
Lime	26·17	7·45	7	27·82
Boracic acid	48·37	33·27	10	49·29
Water	22·12	19·66	18	22·89
Soda	1·57	0·40		
Chloride of sodium	1·77			

Much more boracic acid was extracted from the compound by the action of hot water than by washing with cold water. Its composition may be expressed by the formula $5(CaO + 2BO^3 + 3HO) + 2CaO\,HO$.—Poggendorff's *Annalen*, lxxxvi. p. 561.

On some Double Salts of Cyanide of Mercury.
By G. KOHL *and* A. SWOBODA.

Muriate of Strychnine and Cyanide of Mercury, $C^{42}H^{22}N^{2}O^{4}$, $HCl + C^{2}NHg$.—If hot, rather dilute solutions of neutral muriate of strychnine and cyanide of mercury be mixed together, acicular crystals soon separate; these are soluble with difficulty in cold water, but dissolve readily in hot water and alcohol. The compound, dried at 212° F., gave on analysis—

Carbon	53·87	44 =	264·0	53·18
Hydrogen	4·72	23	23·0	4·63
Nitrogen	..	3	42·0	8·46
Oxygen	..	4	32·0	6·46
Mercury	19·72	1	100·0	20·14
Chlorine.....	..	1	35·4	7·13

Muriate of Berberine and Cyanide of Mercury, $C^{42}H^{18}NO^{9}HCl + C^{2}NHg$, is obtained by adding a hot watery solution of cyanide of mercury to a similar solution of muriate of berberine. On cooling, yellow acicular crystals separate, which are soluble in hot water and hot dilute alcohol, but insoluble in cold water. The salt undergoes no change either in the air or at 212° F. Analysis of the substance dried at 212°:—

Carbon	..	44 =	264·0	50·92
Hydrogen	..	19	19·0	3·66
Nitrogen	..	1	28·0	5·40
Oxygen	..	9	72·0	13·91
Mercury	19·17	1	100·0	19·29
Chlorine.....	..	1	35·4	6·82

Caffeine and Cyanide of Mercury, $C^{16}H^{10}N^{4}O^{4} + 2C^{2}NHg$.—A hot solution of caffeine in alcohol of spec. grav. 0·848, added to a hot solution of cyanide of mercury, gives on cooling colourless acicular crystals. These are soluble with difficulty in cold water and alcohol. They underwent no change at 212° F.; and when dried at this temperature, their analysis gave—

Carbon	..	20 =	120	26·91
Hydrogen.....	..	10	10	2·24
Nitrogen	..	6	84	18·83
Oxygen.....	..	4	32	7·18
Mercury	45·11	2	200	44·84

Muriate of Æthylamine and Cyanide of Mercury, $C^{4}H^{7}N, HCl + 2C^{2}NHg$.—A solution of neutral muriate of æthylamine, evaporated on the water-bath with a watery solution of cyanide of mercury, gives laminar crystals, which are readily soluble in water, with difficulty in cold alcohol, and possess an unpleasant metallic smell. They resist the action of the air, and undergo no change on the water-bath. The analysis of the substance, dried at 212° F., gave—

Carbon..... ..		8 =	48·0	14·39
Hydrogen		8	8·0	2·39
Nitrogen..... ..		3	42·0	12·59
Chlorine..... ..		1	35·5	10·67
Mercury	59·6	2	200·0	59·96

The authors did not succeed in preparing crystalline compounds of cyanide of mercury with piperine, quinine and solanine.—*Ann. der Chem. und Pharm.*, lxxxiii. p. 339.

On the Action of the Ammoniacal Bases upon Oil of Mustard. *By* Dr. HINTERBERGER.

Æthylamine has a very powerful action upon oil of mustard. If the base be passed into oil of mustard, under the influence of cold, until the oil smells of æthylamine, a thick yellow fluid is obtained, which could not be brought to crystallize. With acids it formed no crystallizable salts. When heated in a test-tube, white fumes of a penetrating odour were given off, which condense in oleaginous drops. These have an alkaline reaction, and are coloured blood-red by perchloride of iron. On applying a strong heat, a shining coal remains.

When the syrupy mass is saturated with dry hydrochloric acid gas, dissolved in absolute alcohol, and an alcoholic solution of chloride of platinum added to it, yellow acicular crystals separate. These, when washed with alcohol and water, underwent no change in the air, dissolved with difficulty in water and alcohol, and remained unchanged at 212° F. The analysis of the crystals dried at this temperature gave 28·28 of platinum, according to which the compound is the platinochloride of the æthylic base, *thiosinæthylamine*, $C^{12}H^{12}N^2S^2$, $HCl + PtCl^2$.

As the author did not succeed, in spite of many attempts, in isolating the base thiosinæthylamine in a crystalline form, he endeavoured to prepare sinæthylamine which is homologous with sinamine.

If thiosinæthylamine be mixed with pure, freshly prepared hydrated oxide of lead, and heated until a filtered sample no longer becomes black with hydrated oxide of lead on the addition of potash, and the mass thus obtained extracted first with water and then with alcohol, and the solutions evaporated, a dark yellow syrupy mass is obtained, which after some time becomes nearly entirely crystalline. The crystals are purified by solution in æther. These are crystals of—

Sinæthylamine, $C^{12}H^{10}N^2$.—It has a very bitter taste; dissolves in alcohol and æther, but not in water; its solutions have an alkaline reaction. It melts at 212° F. into a colourless fluid, which, on being touched with a cold glass rod, starts into crystals from the point of contact. It is partially soluble in muriatic acid; bichloride of platinum added to the solution gave reddish-yellow plumose crystals, which, when dried at 212° F., gave on analysis 31·55 per cent. of platinum. The formula of the muriate of sinæthylamine

and chloride of platinum, $C^{12}H^{10}N^2$, $HCl+PtCl^2$, requires 31·24 per cent. platinum.

A solution of sinæthylamine furnishes with a watery solution of perchloride of mercury a white flocculent precipitate. This is

Sinæthylamine-perchloride of Mercury, $C^{12}H^{10}N^2+3HgCl$.—It fuses on the water-bath to a yellow resinous mass, which on cooling sets in a crystalline form. Analysis gave—

Carbon	13·63	12 =	72·0	13·95
Hydrogen	1·82	10	10·0	1·93
Nitrogen	..	2	28·0	5·44
Chlorine.....	..	3	106·2	20·57
Mercury	58·65	3	300·0	58·11

The author did not succeed in preparing crystalline compounds of oil of mustard with methylamine, propylamine and amylamine; a brown syrup-like fluid was obtained. The platinum compounds of these ammoniacal combinations of oil of mustard can however apparently be obtained in a crystalline form.—*Ann. der Chem. und Pharm.*, lxxxiii. p. 346.

Chemical Investigation of the Mexican Honey Ant.
By Charles M. Wetherill, Ph.D.*

Several of these curious insects were handed to me some time since by Dr. Leidy, with the request that I would make a chemical examination of them. I was fearful at the time, from the scarcity of material, and from the endosmosis and exosmosis that had apparently taken place (as the ants had been preserved for some time in alcohol), that I could not arrive at satisfactory conclusions. The difficulties were not, however, as great as anticipated. The following are the results of my experiments:—

The ants were filled with a varying quantity of the honey; in some the abdomen was distended, in others quite flaccid. The liquid also varied, in some being of light amber colour, and in others deeper in hue. Six of the average-sized insects weighed 2·6533 grms., their bodies weighed 0·288 gr. The honey, consequently, of the six ants weighed 2·3653 grms., and the average quantity of honey in a single ant 0·3942 gr. Since the average weight of a single ant is 0·048, it follows that the honey which one of these ants contains on an average is 8·2 times greater than the weight of its body. The density of the ants, when filled with honey, and that of their bodies, was ascertained by weighing in alcohol of density 0·8309, and reducing to water as unity.

The following are the data:—

2·6533 grms. of the ants, with their honey, weighed in alcohol 0·9310; and of the bodies without the honey, 0·288 weighed 0·061 in alcohol. From which the density is calculated, for the ants filled with honey at 1·28, and for the bodies alone 1·05.

The syrup extracted from the ant had an agreeable sweet taste,

* Communicated by the Author.

the odour very much resembling that of the syrup of squills. It reacted slightly acid to blue litmus-paper. When evaporated by the heat of steam, it dried to a gummy mass, which did not exhibit traces of crystallization after standing for a couple of weeks. It was very hygroscopic, becoming quickly soft from the absorption of water from the atmosphere.

The sugar dried, as stated, by steam-heat, dissolved without residue in ordinary alcohol, leaving a residue in nearly absolute alcohol. This residue dissolved in ordinary alcohol completely. The alcoholic solutions were all set aside for several days, for crystallization, with negative results. These alcoholic solutions had exactly the smell of the perfumed bay rum. I call attention to these peculiar odours, as perhaps capable, with additional evidence, of throwing some light upon the origin of the honey.

When exposed for some time *in vacuo* over sulphuric acid, the syrup dries up to a transparent gum-like mass, but without any signs of crystallization during the process. 2·1065 of the syrup, after standing thus *in vacuo* for about two weeks, weighed 1·4425, equal to a per-centage of 68·476 sugar in the syrup. When thus dried, it had the rich sugar-smell of candy made by heating sugar and butter together.

Some of the honey was set aside for crystallization as removed from the insect. After many days it was examined, but no traces of crystallization could be observed either with the naked eye or with the microscope. Some of the honey was examined alone under the microscope with high powers; no crystals were observed, but here and there fragments of organic tissue. Examined by polarized light, some of these stood out in bright relief against the dark ground of the field, and were at first mistaken for fragments of crystals, until a capillary-like tube was observed, which resembled these fragments, and which changed its colour by the rotation of the polarization's plane.

No change could be observed after touching the drop under the microscope with a drop of solution or tincture of iodine.

A drop of the honey in a watch-glass blackened when exposed to a steam-heat with dilute sulphuric acid.

When heated with the blue solution obtained by adding tartaric acid or solution of potash to sulphate of copper, a red precipitate of the suboxide of copper fell.

Chloride of barium, ferrocyanide of potassium and sulphate of copper, added to an aqueous solution of the honey, gave no precipitates either in the cold or by heat.

Nitrate of silver gave in the cold a whitish precipitate, which changed to dark brown by heating.

A portion of the honey heated on platinum foil blackened, gave out fumes and the odour of burnt sugar, leaving a porous coke, which burned off and left an almost imperceptible ash.

A portion of the substance which had been left *in vacuo* for two weeks was taken for analysis by combustion with oxide of copper and chlorate of potash.

As the honey thus dried was not perfectly hard, but of a sticky nature, it was necessary to introduce it into the combustion-tube upon a piece of glass. 0·497 of honey gave 0·306 of water and 0·684 of carbonic acid, corresponding to a per-centage of C=37·525 and H=6·841; O by loss=55·634. This corresponds, as nearly as could be expected, under the circumstances of the analysis, with the formula of crystallized grape-sugar, $C^{12} H^{14} O^{14}$, as may be seen by the following comparison:—

	Analysis.	Anal. starch-sugar by De Saussure.		Calculation.
Carbon	37·525	37·29	12 =	36·363
Hydrogen	6·841	6·84	14	7·071
Oxygen	55·634	55·87	14	56·566

The following analyses may be compared with my results:—
I. Diabetic sugar, by Peligot. II. Sugar of grape, by De Saussure. III. Cane-sugar, by Liebig. IV. Sugar of honey, by Prout.

	I.	II.	III.		IV.
Carbon	36·7	36·71	42·30		36·36
Hydrogen	7·3	6·78	6·45	H }	63·64
Oxygen	56·0	56·51	51·50	O }	

It results, I think, from these experiments, that the honey contained in the Mexican ant is a nearly pure solution of the sugar, so called, of fruits which is in a state of hydration, isomeric with grape-sugar, $C^{12} H^{14} O^{14}$, and differing from grape-sugar in not crystallizing. The phænomena of circular polarization differ in these two named sugars; but the want of sufficient material rendered such comparison impossible. The honey of bees is a mixture of these two kinds of sugar; and as it is obtained from the nectar of flowers containing cane-sugar, the transformation into fruit and grape-sugars must take place in their bodies*. As the ant-honey yields, among its reactions, one of cane-sugar, viz. that of blackening when heated with dilute sulphuric acid, it is possible that it may contain an admixture of cane-sugar, which would account for the imperfect correspondence of the analysis with the per-centage calculated from the formula. It renders also the supposition plausible, that these ants obtain their honey from the same source as the bee.

With regard to the acidity of the honey, want of material prevented any experiments. Can it be formic acid, or is it acetic from the oxidation of the alcohol in which the ants were preserved?

A portion of the alcohol (reacting acid like the honey), neutralized by caustic potash, then distilled with sulphuric acid, gave an aqueous acid liquid, which, on addition of nitrate of silver, gave a whitish precipitate, becoming black on boiling, rendering the supposition of formic acid probable.

* Loewig's Chem. der Org. Verbindungen.

ANALYTICAL CHEMISTRY.

On the Qualitative and Quantitative Determination of Iodine, and its Separation from Bromine and Chlorine by means of Benzine and Nitrate of Silver. *By* E. MORIDE.

BENZINE possesses the property of dissolving iodine wherever it meets with it in a free state. The colour presented by this solution is bright red, which becomes deeper in proportion to the amount of iodine contained in it. When exposed to the air, the iodine is volatilized, and the solution becomes discoloured.

If a few drops of nitrous acid be put into a liquid containing an alkaline iodide, and after the mixture is effected 2 or 3 grms. of benzine be added to it, and the whole strongly agitated, the benzine soon rises to the surface of the liquid, exhibiting a magnificent colour, arising from the iodine which it brings with it. This reaction renders it possible to determine with the greatest ease the presence of 1 milligrm. of iodine in 4 litres of water. Neither æther nor the oils of lavender, citron or turpentine, furnish under similar circumstances such decisive results.

Chloroform, employed either in M. Rabourdin's method or in that of M. Grange, certainly in many cases readily shows the presence of iodine; but its sensibility and the colour which it acquires are far from being so conclusive as the characters offered by benzine. In carefully conducted experiments, I have been able in this way to determine the presence of iodine wherever traces of it were indicated by starch-paste, and the employment of benzine has always appeared to me to furnish most satisfactory results.

I will add to these observations, that if by means of benzine we can separate extremely small quantities of iodine from water, it is also very easy to determine these quantities by nitrate of silver or metallic mercury.

Thus, after washing the iodized benzine repeatedly in distilled water, I take it up in a pipette, and introduce it into a corked tube, in which I agitate it in contact with a few drops of a solution of nitrate of silver or with a known quantity of mercury, until the liquid is completely decolorized.

In the first case, the yellow precipitate of iodide of silver is washed with alcohol of 0·86 spec. grav., thrown on a filter, and treated like chloride of silver which it is intended to weigh.

In the second, the mercury is shaken with the iodized solution, and the augmentation of its weight determined. These results may be checked by dissolving the protiodide of mercury formed in an excess of iodide of potassium.

Bromine, and bromides to which dilute nitric, nitrous or muriatic acids have been added, do not communicate any colour to benzine; the same is the case with chlorine and chlorides. The bromine and chlorine remain dissolved in the water which serves to wash the benzine; they may be separated in the form of a white precipitate by nitrate of silver. Benzine, taking up iodine without possessing

the property of dissolving either bromine or chlorine, enables us therefore to separate iodine perfectly from these two bodies, and to prove in a precise manner the presence of chlorides or bromides in commercial iodide of potassium.—*Comptes Rendus*, Nov. 29, 1852, p. 789.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the use of Burnt Lime instead of Limestone as a Flux in Blast-Furnaces. *By* E. Montefiore-Levi *and* Dr. Emil Schmidt.

The study of the gases formed in blast-furnaces, with which the authors have been engaged for some years, has shown that the use of carbonate of lime as a flux is attended with great loss, and likewise that this loss may be obviated by using burnt lime instead. The gases were taken from a blast-furnace, 54 feet high, at Ougrée, at thirty-two places, 1 foot apart, and the per-centage of carbonic acid determined. The following table contains the results of repeated experiments; I. gives the height above the tuyère, II. the depth below the furnace-mouth, III. the per-centage of carbonic acid:—

	I.	II.	III.		I.	II.	III.
	′ ″	′ ″			′ ″	′ ″	
1	50 4	1 8	9·40	17	29 6	22 6	3·54
2	48 6	3 6	8·51	18	28	24	3·39
3	45 4	6 8	7·01	19	26	26	3·35
4	44 4	7 8	6·29	20	25	27	3·16
5	43	9	5·93	21	23	29	2·81
6	42	10	5·49	22	21	31	1·08
7	41	11	5·01	23	19	33	1·02
8	40	12	4·19	24	17	35	0·06
9	39	13	4·47	25	15	37	0·32
10	38	14	2·22	26	13	39	2·59
11	37	15	1·91	27	11 4	40 8	4·96
12	36	16	3·18	28	9	43	4·78
13	35	17	1·69	29	8	44	0·05
14	33	19	3·47	30	top of hearth		0·86
15	32	20	2·46	31	.. tymp stone		3·10
16	31	21	3·05	32	.. tuyère		10·10

It is evident from the above table that the carbonic acid is formed on the first introduction of atmospheric air, and within a remarkably short distance is reduced to carbonic oxide, for the gas 8′ above the tuyère does not contain a trace of carbonic acid; however, the zone from which carbonic acid is entirely absent is of very limited extent; from 9′ to 10′ above the tuyère the gas again contains carbonic acid, and in no inconsiderable quantity. The authors are of opinion that this carbonic acid results from the reduction of magnetic oxide of iron, or, as the experiments of Stammer have proved, from the carbonization of iron at the cost of carbonic oxide.

The per-centage of carbonic acid in the gas increases at a height of 10′ or 11′ above the nose pipe, above which point a second reaction takes place between the carbon of the fuel and the carbonic acid, the per-centage of the latter decreasing up to a height of 15′ above the tuyère, where it is 0. From this point it again increases in quantity, and rapidly, for at a height of 30′ it amounts to 3·5 per cent. The authors ascribe this considerable increase of carbonic acid solely to the decomposition of the limestone used as a flux. Their analyses of the gas according to the eudiometric process of Bunsen have strengthened this opinion, and the result of Ebelmen's interesting experiments on the reduction of ores in blast-furnaces furnishes a full confirmation of it.

Ebelmen exposed ore (a calcareous brown ironstone), in an appropriate apparatus, to a high temperature, at different heights of the shaft of a blast-furnace, with the following results:—

		The ore at			
		8′	13′	15′	17′
Constituents.	Original ore.	below the furnace-mouth.			
Carbonate of lime....	36·8	41	40·6	26·6	
Caustic lime.....	..	..	..	4·0	37·4
Peroxide of iron	36·2	37	27·8	24·1	
Protoxide of iron	..	traces	12·7	17·5	30·2
Metallic iron.....	..	..	..	..	10·0

These experimental results are sufficient to show that Ebelmen's experiments agree with the observations of the authors, for at a depth of 13′ (half the height of the furnace) the disengagement of carbonic acid did not take place, although the peroxide of iron was already reduced to protoxide.

If the numbers in the above table are examined more closely, they afford proof of a reaction of great importance, and one which might not have been expected at such a height in the furnace. Thus after the increase of the per-centage of carbonic acid to 3·5 in consequence of the decomposition of carbonate of lime, it again diminished in proportion to the increased height, until at a point from 37′ to 39′ above the tuyère it amounted to only 1·69 or 1·91 per cent., which may be regarded as about the quantity present in the gas before the decomposition of the carbonate of lime. Above this point the quantity of carbonic acid increases again up to the furnace-mouth, and indeed with tolerable rapidity and regularity, in consequence of the reduction of peroxide of iron to protoxide by the action of carbonic oxide.

The authors are of opinion that the carbonic acid, which is disengaged from the limestone at a height of 27′ above the tuyère, and again disappears almost entirely at a height of 39′, reacts within this space upon the ignited coke, taking up part of its carbon; and an examination of the analyses confirms this view.

Although other observers who have studied the composition of the gases from blast-furnaces have not collected them at so many different heights, still their analytical results clearly indicate that in

the furnaces from which they took the gas, the carbonic acid derived from the limestone was at least partially reduced to carbonic oxide, as at Ougrée. Bunsen and Playfair found the gas from a blast-furnace at Alfreton, worked with crude bituminous coal, to consist of—

	Depth in the furnace.	Per-centage of carbonic acid.
	23′ 〃	8·19
	20	10·83
	17	11·43
	14	9·10
At Vekerhagen..	11 3	7·57
	8 3	3·06
At Bacrum	16 1	8·05
	13 5	4·27

If these data furnish sufficient evidence in favour of the assumption that the carbonic acid disengaged from the limestone does not directly pass off through the furnace-mouth, but is chiefly converted into carbonic oxide at the cost of the fuel, it may be ascertained by calculation what quantity of coke is consumed in consequence of this reaction, and what loss of temperature attends the conversion of the carbonic acid of the limestone into the gaseous state. For the determination of the first question, it may be assumed that the temperature to which the limestone is exposed equals that at which gold melts, 2012° F; the specific heat of carbonic acid is 0·22; the quantity of limestone consumed in the furnace at Ougrée during twenty-four hours is about 20,000 kilogrms., containing about 8000 kilogrms. of carbonic acid. Consequently the quantity of caloric absorbed during twenty-four hours amounts to $8000 . 0{\cdot}22 . 1100 = 1{,}936{,}000$, which, taking the heating power of coke at 6000, corresponds to the quantity of heat developed by the combustion of 322 kilogrms. of coke. In the conversion of carbonic acid into carbonic oxide, 1 equiv. of carbon is assimilated, 275 parts of carbonic acid are converted into carbonic oxide by combining with 75 parts of carbon, and the 8000 kilogrms. of carbonic acid in the limestone would require for conversion into carbonic oxide 2173 kilogrms. of carbon, about equivalent to 2500 kilogrms. coke with 11 per cent. ash.

It then remains to be determined whether this change is accompanied by depression or elevation of temperature, for which purpose the following facts must be considered. Dulong found that the quantity of heat disengaged in the conversion of 1 kilogrm. of carbon into carbonic oxide is much less than that disengaged in the conversion of an equivalent of carbonic oxide into carbonic acid, although the same quantity of oxygen is required to convert the carbon into carbonic oxide, or the carbonic oxide into carbonic acid; for as carbonic oxide (CO) consists of 0·43 C and 0·57 O, 1 kilogrm. of carbon produces $\frac{1}{0{\cdot}43} = 2{\cdot}325$ kilogrms. of carbonic oxide, which on combustion developes $2{\cdot}325 . 2488^{*} = 5784$ heat units, conse-

* The relative heating power of carbonic oxide.

quently the conversion of carbon into carbonic oxide is accompanied by the development of only 7150–5784=1386 heat units.

If carbonic acid is converted into carbonic oxide by passing over ignited carbon, the action is essentially twofold, a combination of carbon with oxygen, and a decomposition of carbonic acid into carbonic oxide and oxygen ; the former is accompanied by development of heat, the latter by absorption of heat. The practical question to be decided in the present instance is, which of these two calorific changes preponderates?

According to the above calculations 8000 kilogrms. carbonic acid require for conversion into carbonic oxide 2173 kilogrms. of carbon, and the quantity of heat developed in the combination of this quantity of carbon with 1 equiv. of oxygen is 2173 . 1386=3,011,778 heat units. At the same time, however, these 8000 kilogrms. of carbonic acid are reduced to 5092 kilogrms. of carbonic oxide by the action of the carbon, a change which is accompanied by the absorption of a quantity of heat equal to that developed by the combustion of the latter gas, *i. e.* 5092 . 2488=12,667,896 heat units. Consequently deducting the 3,011,778 heat units developed in the oxidation of carbon from the total number of heat units absorbed in the reduction of carbonic acid to carbonic oxide, there still remains a loss of temperature equal to 9,656,118 heat units, equivalent to the heat developed by the combustion of 1609 kilogrms. of coke.

These considerations led the authors to employ burnt lime in working blast-furnaces, and thus to obviate the loss of heat. The experiment was commenced at Ougrée in July 1849. During the first few days the results were unsatisfactory, the management of the furnace was difficult, and the slags black and pasty. Subsequently, when taking into account the impurities of ordinary limestone, 63 parts of burnt lime were substituted for 100 parts of limestone; the working of the furnace, until it was let out at the beginning of 1851, was continually regular and good; during these eighteen months the most satisfactory results were obtained. The saving of coke and increase of production were, as the experimenters anticipated, very evident; moreover, the raw iron was of better quality, and all the interior parts of the furnace, especially the tymp stone, remained in a much better state of preservation than when limestone was used. The following table gives the quantities of coke consumed, in the production of 100 kilogrms. raw iron, in the above-mentioned furnace, during the four months before and the four after the alteration of the charging, all other conditions remaining the same:—

With limestone.		With burnt lime.	
1849. March ..	150·0 kilogr.	1849. July	142 kilogr.
April ..	154·5 ...	August....	138 ...
May....	156·5 ...	September	133 ...
June....	151·5 ...	October ..	139 ...
Average quantity	153·2 kilogr.	Average quantity	137·75 kilogr.

Average quantity consumed with limestone.. 153·20 or 100 p.c. coke.
Average quantity consumed with burnt lime 137·75 or 90 p.c. coke.
Difference.... 15·45 or 10 per cent.

The practical saving is therefore 10 per cent., which corresponds tolerably well with the theoretical results.

The experiment was repeated in 1850, in a second blast-furnace, with the same favourable result of increased production, saving of fuel and easier working. The following table shows the quantity of coke consumed for every 100 kilogrms. of raw iron, and the production during the first six months (reckoned at twenty-eight days). The figures in the first column refer to the furnace in which limestone alone was used; the second column to the first-mentioned furnace, in which burnt lime alone was used; and the third column to the second furnace, in which limestone was used for three months, and burnt lime for the next three months. All three furnaces are constructed alike, smelt the same ore, and produce the same kind of iron:—

	Quantity of coke in kilogr. consumed for 100 kilogr. raw iron.			Reduction during twenty-eight days in kilogrammes.		
	I. With limestone.	2. With burnt lime.	3. With limestone.	1. With limestone.	2. With burnt lime.	3. With limestone.
April	165	145	163	436,000	601,000	459,000
May	165	147	159	447,000	582,000	461,000
June	160	147½	164	477,000	588,000	488,000
			With burnt lime.			With burnt lime.
July	161	146½	149¾	462,000	555,000	537,000
August	158¾	145	146	465,000	536,000	552,000
September	153	147¾	146	477,000	577,000	600,000
Mean	160½	146¼	154⅔	461,000	573,000	516,000
Average from April to June			162	..	..	469,000
Average from July to Sept.			147¼	..	..	563,000

The very regular and uniform results given in this table show that by the use of burnt lime the consumption of coke for every 100 kilogrms. of raw iron was reduced by 14 to 15¾ kilogrms., while at the same time the production of iron increased within a certain period as much as 22 or 24 per cent.

Hitherto the opinion of metallurgists with regard to the use of burnt lime was rather unfavourable than otherwise; but since the above experiments were made at Ougrée, it has been employed with good results in England and Wales, among other places at Abershyne, where the results obtained were still more satisfactory than at Ougrée, inasmuch as the saving of coke effected by this means amounted to 12 kilogrms. for every 100 kilogrms. of limestone which was replaced by 63 kilogrms. of burnt lime.

New lime-kilns have recently been built at Ougrée; burnt lime has been employed there for two years and a half, and with uniform results, for which reason the authors recommend its general application, from a thorough conviction of the advantage to be gained. The entire saving, inclusive of the expense of burning the limestone, is stated by them to amount to 30,000 francs annually for each furnace.—*Zeitschrift des österr. Ingenieurvereines*, 1852, p. 145–150.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Sinapine. *By* L. von Babo *and* M. Hirschbrunn.

From dry white mustard, which has been freed from oil by treatment with æther, absolute alcohol extracts very little sinapine, but a brown sulphur compound, which is precipitable by æther and another compound of sinapine, which is thrown down by sulphocyanide of potassium as sulphocyanide of sinapine (sinapine). When the mustard has been so far exhausted by the alcohol that this only acquires a pale yellow instead of a golden-yellow colour, the residue is decocted with alcohol of spec. grav. 0·833; this contains all the sinapine, which may be obtained crystallized by evaporation of half the fluid. From the last mother-liquor the sinapine is precipitated by sulphocyanide of potassium. In this manner 0·5 grm. of sinapine is obtained from 1 lb. of mustard.

This method may serve for the preparation of small quantities of sinapine, but is not adapted for its production on the large scale. In operating with 25 lbs. of mustard, it is better to use it in powder, and to free it from oil by pressure in an oil-mill. The residue is extracted first with cold, and afterwards with hot alcohol, the extracts mixed, about three-fourths of the alcohol driven off on the salt-bath, and the residue allowed to cool. If the process be properly conducted, this residue on cooling will separate into two nearly equal strata,—one of oil, the other of solution of sulphocyanide of sinapine. Sometimes the lower stratum soon after cooling forms a yellowish-brown crystalline jelly of sulphocyanide of sinapine; this effect can also sometimes be produced by the addition of a few drops of water, but it generally forms a fluid of a syrupy consistence, which only deposits the sinapine on further evaporation in the most careful manner. The oil is now separated from the lower fluid by a siphon. In this everything depends upon exactly hitting the point at which the fluid possesses the proper degree of concentration. If it be not sufficiently evaporated, much sinapine remains dissolved in the oil, which still contains alcohol. This can only be separated with difficulty; the best process is to add to the oil, previously warmed, some solution of sulphocyanide of potassium in alcohol, by which means the sulphocyanide of sinapine may be brought to crystallize in a few days. On the other hand, if too much of the alcohol be driven off, the sinapine becomes decomposed, or products are formed which prevent crystallization.

The sulphocyanide of sinapine thus procured is first dried, the

mass moistened with alcohol, and again dried. The alcohol removes a brown substance, which prevents the crystallization of the sulphocyanide of sinapine. Lastly, the mass is pressed. From the mother-liquor (not from the original fluid) still more sulphocyanide of sinapine may be precipitated by sulphocyanide of potassium. The sulphocyanide of sinapine is purified by recrystallization from alcohol of spec. grav. 0·833, and decoloration by animal charcoal.

Pure *Sulphocyanide of Sinapine* (sinapine), $C^{34}H^{25}N^{2}S^{2}O^{10}$, has, as already stated by Winckler, the appearance of crystallized sulphate of quinine; it is soluble with difficulty in cold water and alcohol, but dissolves readily in both fluids when hot; in æther it is nearly insoluble. The watery and alcoholic solutions are always of a yellowish colour, even when they are prepared from perfectly colourless materials; on the addition of a drop of an acid, however, they become nearly colourless. The hot saturated watery or alcoholic solution sets on cooling into a mass of crystals. Pure dried sinapine may be heated in a test-tube to 266° F. without undergoing any change. It melts into a yellow fluid, which on cooling solidifies into a glassy mass without any traces of crystallization. At a higher temperature it becomes brown, and evolves fumes of a disagreeable odour, which however has no resemblance to that of sulphuret of carbon, sulphocyanic acid or sulphuretted hydrogen. On further heating, vapours of an alkaloid (perhaps methylamine) are evolved; then follow gases and empyreumatic oils, which burn with a bright flame with formation of sulphurous acid, whilst a shining coal remains.

Heated on platinum foil, it burns without residue. Concentrated sulphuric acid dissolves it readily with the assistance of heat, producing carbonization and the evolution of sulphocyanic acid, the fumes of which may be recognized by their reaction with iron. On evaporation with diluted sulphuric acid, sulphocyanic acid is also evolved. If the fluid be allowed to cool for some time, it sets into a gelatinous mass, from which, after long standing, acicular or laminar crystals are deposited. Concentrated muriatic acid also dissolves it with evolution of sulphocyanic acid. By careful evaporation, a crystalline residue is left. Dilute muriatic acid dissolves it somewhat more readily than water. On cooling, the greater portion recrystallizes unchanged. Brought into contact with nitric acid, it instantaneously acquires a dark red colour. On heating, this colour is changed to yellow: the fluid then contains sulphuric acid, as may be ascertained by means of baryta salts. Alkalies, lime-water, and baryta-water dissolve the substance immediately with an intense yellow colour. The same colour is also produced by the carbonates of the alkalies and earths, by basic acetate and pure oxide of lead. The reaction is extremely delicate, and is also produced by most of the alkaloids, as has already been observed by Winckler. A little tobacco-smoke, blown into a test-tube containing a solution of the substance, produces it. If an acid be added to the alkaline solution, the sulphocyanide of sinapine is immediately thrown down unchanged if the concentration be sufficient; if, on

the other hand, the alkaline solution be boiled, it is decomposed, and on the addition of an acid a heavy crystalline precipitate of a new substance is produced. On boiling its solution in baryta-water, a heavy yellowish baryta compound is precipitated, whilst the fluid becomes almost perfectly colourless; the precipitate contains no carbonate of baryta, and on the addition of muriatic acid is decomposed into chloride of barium and the above-mentioned crystalline body. The solution contains sulphuric acid. Analysis gave:—

Carbon	56·01	55·16	55·09	34	= 204	55·29
Hydrogen	6·88	6·88	6·75	25	25	6·77
Nitrogen.....	6·91	7·93	7·80	2	28	7·58
Sulphur	8·81	9·13	..	2	32	8·67
Oxygen	..	..	..	10	80	21·69

This analysis differs from Henry and Garot's analysis of sinapine, which, according to the calculation of Pelouze, gives 57·920 carbon, 7·795 hydrogen, 9·940 nitrogen, 9·617 sulphur, and 19·688 oxygen.

Sinapic Acid, $C^{22} H^{12} O^{10}$, is formed from the sulphocyanide of sinapine when this is boiled with alkalies. The addition of acids separates the resulting organic acid as a precipitate. This is collected, and purified by recrystallization from its solution in boiling alcohol of spec. grav. 0·912. The alcoholic solution acquires a brown colour on exposure to the air for a considerable time.

Sinapic acid is very difficult of solution in cold, but dissolves more readily in hot water; it dissolves with difficulty in cold, but readily in hot alcohol, from which it crystallizes on cooling; it is insoluble in æther, nearly insoluble in acids; it forms compounds with the alkalies and metallic oxides, those with alkalies being readily soluble and crystallizable, those with earths and metallic oxides difficult of solution. All these compounds, with the exception of the baryta salt, decompose very readily. Analysis:—

Carbon	58·67	58·92	22	= 132	58·93
Hydrogen	4·87	5·67	12	12	5·35
Oxygen	..	..	10	80	35·72

Sinapate of Baryta, $C^{22} H^{10} O^{8}$, 2BaO, is obtained when the acid, or even sinapine itself, is boiled with an excess of baryta-water without access of air, rapidly filtered, and the residue washed with water free from carbonic acid; it is also produced by precipitating the sinapate of ammonia with chloride of barium. Analysis:—

Carbon	36·37	36·54	22	= 132·0	36·80
Hydrogen.....	3·06	2·74	10	10·0	2·78
Oxygen.....	..	..	8	64·0	17·82
Baryta	24·09	42·97	2	152·9	42·60

The neutral *sinapates of potash, soda* and *ammonia*, when exposed in solution to the atmosphere, become coloured in consequence of the oxidation of the salts; the two former turn first green, and afterwards brown; the ammonia salt becomes reddish-brown. The solution of the potash salt, when absolute alcohol is added to it, lets fall iridescent laminæ, which become rapidly changed as soon as the

alcohol is removed. The neutral potash salt furnishes a white precipitate with chloride of calcium, chloride of barium and solution of alum. On the addition of liquid chlorine, the precipitate acquires a rose colour, and afterwards becomes of a dusky violet tint. Chloride of iron gives a rose-coloured, or sometimes a fine purple-red precipitate. If a slight excess of chloride of iron has been employed, or a portion of the precipitate has been dissolved by muriatic acid, ferridcyanide of potassium shows the presence of protoxide of iron in the supernatant fluid. The red colour of the precipitate appears therefore to be produced by an oxidation of the acid, which is also indicated by the behaviour of the aluminous salt. The precipitates given with copper and lead salts also change rapidly assuming a green or brown colour. The salts of mercury and silver, which at first appear colourless, are decomposed very rapidly, especially on the addition of an alkali, with separation of the metal. Gold is immediately reduced from its chloride.

When heated in a test-tube, the acid fuses at about 302°–392° F., and sets on cooling in a crystalline form. Subsequently a colourless oil distils off, whilst the residue acquires a brown colour. This oil does not set in the air, and does not change its colour; the residue, however, in the course of a few hours becomes of an intense red. A crystalline yellow substance, which scarcely reddens when exposed to the air, and is difficult of solution in water, is produced both in the oil and in the residue when exposed to ammoniacal gas. The acid behaves with nitric acid exactly like sinapine. Oxalic acid and a new nitrogenous substance appear to be formed. Liquid chlorine communicates to the acid, especially when warmed, an intense rose colour, which afterwards becomes purple-red without dissolving an appreciable portion of it.

The authors show, that in these reactions, as well as in its composition, the acid agrees most nearly with the erythric acid of Stenhouse; nevertheless it differs from that acid in its behaviour under dry distillation and in its baryta salt.

Sinkaline, $C^{10}H^{13}NO^3$, is the third product obtained together with sinapic acid and sulphuret of cyanogen, by boiling sinapine, with baryta-water. This fluid is acidified with sulphuric acid, and the sulphocyanogen removed by the addition of sulphate of iron and copper. The excess of these salts is got rid of by baryta, and lastly the excess of baryta by means of carbonic acid. If the solution be now evaporated, it contains nothing but the deliquescent carbonate of sinkaline, which, on the addition of acids, evolves its carbonic acid with violence.

Pure sinkaline is readily obtained from its muriate by digesting this with oxide of silver. It forms a colourless or slightly brownish mass of crystals, which when exposed to the air immediately attracts water with increase of temperature, and deliquesces; in air containing carbonic acid it passes into the carbonate. In this respect its behaviour perfectly resembles that of hydrate of potash, to which moreover it scarcely yields in causticity. It is volatile without decomposition; when heated, it leaves behind a coal, whilst it diffuses

the odour of methylamine. Its fumes burn with flame. Like potash, it throws down all metallic oxides; baryta, lime, and oxide of mercury not excepted. Alumina and oxide of chrome are dissolved by it in excess, and the latter is precipitated by heat just as from the solution of oxide of chrome in potash. It dissolves sulphur, forming sulphuret of sinkaline and sulphuric acid salts. The solution is precipitated by acids, with evolution of sulphuretted hydrogen and separation of milk of sulphur.

The compounds of the new base with muriatic, sulphuric, nitric, and carbonic acids are also deliquescent.

The *platinum double salt*, $C^{10} H^{15} NO^2 Cl^3 Pt$, crystallizes, after the evaporation of solution of muriate of sinkaline and chloride of platinum, in beautiful, orange-coloured, rhombic prisms. By very gradual evaporation thin six-sided tables of half an inch in diameter are obtained. At 230° F. the air-dried salt lost 5·23 per cent. of water =2HO. The analysis of the salt, dried at 230° F., gave—

Carbon	19·73	19·58	10 =	60·0	19·34
Hydrogen	5·16	5·10	15	15·0	4·83
Nitrogen.....	..	..	1	14·0	4·73
Oxygen	..	..	2	16·0	4·96
Chlorine.....	..	..	3	106·5	34·33
Platinum.....	31·36	..	1	98·7	31·81

The *gold double salt*, $C^{10} H^{15} NO^2 Cl^4 Au$, is precipitated from the watery solution as a yellow crystalline powder. Washed with cold water, in which it is difficult of solution, it crystallizes from its solution in boiling water in acicular and laminar crystals united in a plumose form. Analysis gave:—

Carbon.....	13·63	10 =	60·0	13·50
Hydrogen	3·38	15	15·0	3·38
Nitrogen	..	1	14·0	3·15
Oxygen	..	2	16·0	3·61
Chlorine	..	4	142·0	32·02
Gold.....	44·54	1	196·7	44·34

According to the reactions which are peculiar to the new base, it belongs to the fourth series of Hofmann's ammonia bases, but differs from the other bases of that series by the oxygen contained in the platinum and gold salts.

The *sulphocyanide of sinapine*, $C^{34} H^{25} N^2 S^2 O^{10}$, appears consequently to change in the following manner when treated with baryta-water:—

$$C^{34} H^{25} N^2 S^2 O^{10} + 3BaO = C^2 NS^2 Ba + C^{10} H^{15} NO^3 + C^{22} H^{10} O^8, 2BaO.$$

It therefore still remains doubtful whether sinapine is to be looked upon as the sinapate of a conjugate base formed of sinkaline and sulphocyanic acid, like the cyanharmaline of Fritzsche or the cyananiline of Hofmann, or whether it must be regarded as the sulphocyanide of an alkaloid, containing the elements of sinkaline and sinapic acid. For deciding this question, it is of great importance

that two modifications of sulphocyanide of sinapine exist, of which one, like every soluble sulphocyanide, immediately reddens the salts of peroxide of iron, whilst the other only produces this reaction when warmed. The preceding experiments are made with that modification which immediately reddens the iron salts.

The authors received a specimen of that which does not redden the salts of iron from Will, who was the first to observe the difference between the two modifications. With all other reagents it behaved exactly like the preceding. Will has also already observed, from a statement of Dollfuss, that sulphocyanide of silver is precipitated from sulphocyanide of sinapine by nitrate of silver. Dollfuss has also observed a new reaction, which moreover belongs to both modifications, and leaves little doubt that sinapine must be regarded as the sulphocyanide of a conjugate alkaloid, to which the name of *sinapine* must be specially applied. This is as follows:—

If some sulphuric acid be added to a hot concentrated solution of the substance in alcohol of spec. grav. 0·833, a compound is thrown down, on cooling, in rectangular laminæ; this is an acid salt of the base, of which sulphocyanide of sinapine is to be regarded as the sulphocyanogen compound. It may be completely separated from the sulphocyanic acid and the excess of sulphuric acid by washing in absolute alcohol; after several recrystallizations from water and alcohol, and drying at 212° F., it has the composition $C^{32}H^{26}NO^{12}, 2SO^3$, as shown by the following analysis:—

Carbon	46·99	32 =	192	47·06
Hydrogen.....	6·37	26	26	6·37
Nitrogen	..	1	14	3·43
Oxygen.....	..	12	96	23·53
Sulphuric acid	19·82	2	80	19·61

This salt is consequently formed in the following manner:— $C^{34}H^{25}N^2S^2O^{10}+2HO+2SO^3=C^{32}H^{26}NO^{12}2SO^3+C^2NS^2H$, or $C^{32}H^{25}NO^{11}SO^3+C^2NS^2H$. In the crystalline state it still contains 4 atoms of water of crystallization, which it loses at 230° F. This salt has a strong acid reaction, and is readily soluble in water and boiling alcohol, from which the greater part of it crystallizes on cooling. It is nearly insoluble in æther.

This base, $C^{32}H^{26}NO^{12}$, which will now be called *sinapine* (whilst hitherto the sulphocyanide has been also included under that denomination), could not be isolated by alkalies, on account of the readiness with which it is decomposed. The authors have nevertheless investigated the behaviour of its solution and of some of its salts. They obtained the solution of pure sinapine by adding to the solution of its above-described sulphate so much baryta-water (from a burette) that only the second atom of sulphuric acid was thrown down; this point is known from the fact, that the solution immediately becomes of an intense yellow colour on the addition of the first drop of baryta-water beyond the proper quantity. If now an additional quantity of baryta-water equal to that

already employed be poured in, the sulphuric acid will be completely thrown down.

This solution of the base has a distinct alkaline reaction, and precipitates the oxides from many metallic salts; salts of mercury give a yellow, salts of copper a green, and salts of silver a grayish-brown precipitate. On exposure to the air or heating, these precipitates present the same phænomena of reduction as the salts of sinapic acid. From chloride of gold, metallic gold is precipitated. On evaporation, the colour of the solution of sinapine passes through green and red to brown, whilst an amorphous residue remains. In this respect it behaves like the solution of a salt of sinapic acid. No sinapine is separated from this solution by the addition of alcohol or æther; for as it is very difficult of solution in æther, that substance does not take it from the water, nor does it undergo any precipitation by alcohol.

The attempted separation of the base by treating its sulphate with precipitated hydrated oxide of lead was unsuccessful, because the sinapine enters into combination with the latter, forming a gelatinous mass, which is somewhat soluble in boiling water. The same compound appears also to result from the boiling of finely-powdered litharge with sulphocyanide of sinapine. If the solution of acid sulphate of sinapine be boiled with an excess of baryta-water or potash, it immediately splits into a sinapic acid salt and sinkaline.

The neutral sulphate of sinapine (in the restricted sense), obtained as above mentioned, forms by evaporation of its solution a colourless mass of crystals, which are very readily soluble. By careful addition of chloride of barium or nitrate of baryta to the solution, the muriate and nitrate of sinapine may be obtained. Both crystallize on evaporation in fine acicular crystals, which are very readily soluble. If one of these salts be warmed with a solution of sulphocyanide of potassium, sulphocyanide of sinapine is regenerated, and crystallizes with all its properties on the solution becoming cool. On mixing the solution of the muriate with chloride of platinum, a resinous precipitate immediately falls to the bottom. This is decomposed on the application of the least heat, becoming brown and depositing a new flocculent precipitate.

The nitrate is also obtained, together with sulphocyanide of silver, when a boiling solution of sulphocyanide of sinapine is precipitated by nitrate of silver.

Sinapine (in the restricted sense) can therefore be separated from the sulphocyanide of sinapine (sinapine, sulphuret of sinapine) by all those reagents which set free sulphocyanic acid from sulphocyanides, if an excess of alkali, by which the sinapine would be decomposed, be avoided.

In some experiments in which the authors allowed synaptase to act upon sinapine, they have hitherto obtained no decisive result; the sinapine appeared to remain for the most part unchanged. It appears, however, as has already been ascertained by Simon, that the yellow mustard contains another compound which is rich in sulphur, and which plays a more important part in the formation of

the pungent matter, and perhaps also of the oil of mustard, than the sulphocyanide of sinapine.—*Ann. der Chem. und Pharm.*, lxxxiv. p. 10.

On Anhydrous Caprylic and Pelargonic Acids. *By* L. Chiozza.

In a preceding communication the author laid before the Academy the results of some experiments on anhydrous valerianic acid *. Wishing to increase the number of facts serving to support M. Gerhardt's theory as to the constitution of the anhydrous monobasic acids, he extended his researches to caprylic and pelargonic acids. He thinks that the selection of similar examples amongst the organic acids will tend to modify the opinions of chemists as to the relations between these acids and the corresponding anhydrous acids.

The caprylic acid was obtained from butter of the cocoa-nut by M. Fehling's process; the caproic acid which accompanies it was separated by neutralizing the mixture with caustic baryta, and submitting to repeated crystallization the salt which is first deposited. This salt is very readily attacked by oxychloride of phosphorus, which renders it unnecessary to transform it into the potash salt; the anhydrous caprylic acid is extracted from the mixture by æther free from alcohol. The ætherial solution is treated with a weak solution of potash, and after drying upon chloride of calcium, the æther is driven off on the water-bath. The acid thus obtained gave on analysis numbers exactly corresponding with the formula

$$C^{16}H^{30}O^3 = \left\{\begin{matrix} C^8H^{15}O \\ C^8H^{15}O \end{matrix}\right\} O.$$

It is a limpid oil, of great mobility, greasy to the touch, and lighter than water. It has a nauseous odour; when heated, it emits fumes which irritate the throat. Placed in a mixture of snow and salt, it forms a white mass, which only appears crystalline when magnified. It again becomes fluid some degrees below 32° F. It boils at about 536° F.; in distillation this temperature reaches 554° F. at the end, whilst the residue in the retort becomes darker and transformed into empyreumatic products of a very fœtid odour.

Brought into contact with aniline, the mixture becomes slightly heated, and congeals after some days into a butyraceous mass. The author hoped to have obtained *caprylanilide* in this manner; but if it exists in this mixture, its purification was so difficult that he abandoned the attempt.

Boiling water has no action on anhydrous caprylic acid; long contact with moist air produces a partial hydration.

Solution of potash of moderate strength converted it, by the assistance of heat, into caprylate of potash.

Thus whilst anhydrous acetic acid is transformed into acetic acid by the simple contact of water, and anhydrous valerianic acid is rapidly hydrated by exposure to moist air, anhydrous caprylic acid requires the intervention of caustic alkali to convert it into ordinary

* Chem. Gaz., p. 52 of the present volume.

caprylic acid. This is still more distinctly the case with anhydrous pelargonic acid, which is prepared exactly like the preceding.

It exhibits the appearance of a colourless oil, lighter than water; when cold, it has a faint odour like that of rancid butter; but when placed in boiling water, it communicates to the vapour an aromatic and slightly vinous odour, which is not disagreeable. Heated by itself on a glass plate, it emits acid fumes, which smell like burnt fat. At 32° F. it forms a mass of fine needles, which again become liquid at 41° F. Analysis gave results agreeing with the formula—

$$C^{18}H^{34}O^3 = \left\{\begin{matrix} C^9H^{17}O \\ C^9H^{17}O \end{matrix}\right\} O.$$

The author also prepared the pelargonate of benzoyle—

$$C^{16}H^{22}O^3 = \left\{\begin{matrix} C^7H^5O \\ C^9H^{17}O \end{matrix}\right\} O,$$

a clear oil, heavier than water, and resembling in its physical properties the anhydrous acid; a little below 32° F. it is transformed into a butyraceous mass, which reacquires its fluidity as soon as it is taken from the freezing mixture. When heated, it emits very acrid vapours, and is decomposed at an elevated temperature into anhydrous benzoic and pelargonic acid, with some other products of the decomposition of the latter. The change which this substance undergoes by the action of heat may be shown by exposing it afterwards to cold; a crystalline precipitate is formed, which is only dissolved on shaking the mixture. A drop of it, left in moist air, becomes filled with fine needles of benzoic acid. Alkalies convert it readily into benzoic and pelargonic acids.—*Comptes Rendus*, Dec. 13, 1852, p. 865.

On the Permeability of Metals to Mercury. *By* J. Nicklès.

In an interesting memoir on the permeability of metals to mercury, by Prof. Horsford, this author establishes the fact of the permeability of tin, lead, gold, silver, zinc and cadmium, and contests that of copper and brass.

The negative results which this chemist has obtained with copper and brass have evidently proceeded from the process which he has followed; for some time since, while engaged in my researches on magnetization, I observed positive facts to the contrary. I was using at this time a Bunsen's battery with zinc exterior. The connecting pieces of copper were riveted to the zinc, and on amalgamating the latter metal, it often happened that the mercury spread itself over the copper in contact with the zinc; and after a certain time the metal of the connecting pieces became brittle, and had on breaking a white colour. It was obviously no longer copper, but an amalgam of this metal.

This fact had too important a bearing on the amalgamation of zinc, which occupied me at that time, to be allowed to pass without examination. The experiments which I made on this subject led to

the general conclusion, that the metals which absorb mercury are permeable by it, and communicate this property to the alloys which contain a certain proportion of permeable metal. The metals on which I have operated are zinc, iron, cadmium, tin, copper, lead, antimony, silver, gold and platinum. The manner of experimenting was suggested by the fact which had led to the researches. With a stylet I traced a line or furrow on the plate under experiment, and placed a little mercury in this furrow. In order to hasten the amalgamation, I introduced before the mercury a drop of bichloride of mercury acidified with hydrochloric acid. By this means the amalgamation takes place instantly, and the surface is fitted to retain at once the quantity of mercury necessary for the effect I wished to produce.

A plate of zinc, a millimetre thick, is immediately attacked, and at the end of a minute it is cut in two in the direction of the furrow. A thicker plate requires more time and a deeper scratch on its surface; with a thickness of 6 millims. the plate took ten minutes and a little effort to break it; but in all cases the fracture was neat and in the direction of the scratch or furrow.

After zinc comes cadmium and tin, then lead, silver, gold, and finally copper. All of these metals become amalgamated; the mercury infiltrates after a time more or less long, and renders them brittle. No permeability has been detected in iron, antimony and platinum, and these metals form no amalgam. Daniell found a bar of platinum free from mercury, that had been for six years in contact with it, and to this time no amalgam of iron has been reported.

There exists, it is true, an amalgam of antimony; but, according to Wallerius, when this amalgam, of a pasty consistence, is triturated in the air, or when agitated with water, it loses its antimony in the form of a black powder*.

As to the action of mercury on metals, this fact at least is established,—the resistance of some to amalgamation and the easy amalgamation of others. We have also shown that the permeability takes the same direction, and we may conclude therefore that the alloys will participate in these qualities in the order of their composition. In fact, a plate of bronze 5 millims. thick may be cut in two by mercury after ten minutes of contact, and a plate $\frac{1}{2}$ a millim. thick yields instantaneously. On amalgamating a strip of brass, it may after a few minutes be reduced to fragments between the thumb and finger. A plate of 4 millims. required ten minutes to cut it in two. An alloy, formed of equal parts of antimony and tin, did not appear to be impressed by the mercury. Chaudet's alloy (3 or 4 per cent. of antimony and 96 to 97 of tin), very elastic in its pure state, amalgamates instantly, and is easily cut off.

It is here seen, that if the permeability of brass and copper for mercury is not established by the process, based on *capillarity*, followed by Prof. Horsford, we may still make this property evident by an inverse course, that is by inducing *infiltration*.

* It should be borne in mind, in connexion with this subject, that mercury also is reduced to a black powder by agitation in the air.

As these experiments were made only incidentally, and were not intended to be published, I have not attempted to give them precision. Nevertheless the facts which have been mentioned above are well established, for I have been accustomed to use this process for dividing plates of zinc or sheets of brass in my experiments on electro-magnetism.—Silliman's *Journal*, January 1853.

On the Allotropic Modification of Oxide of Cobalt.
By F. A. Genth.

One of my students, Mr. Edwin L. Reakirt, has discovered the allotropic modification of oxide of cobalt, corresponding in all its properties with the allotropic modification of oxide of nickel, which I detected several years ago*. It was obtained accidentally by the decomposition of the carmine chloride of my cobalt bases (Fremy's hydrochlorate of roseocobaltiaque) by heat; and after dissolving out the chloride of cobalt, it remained pure. It occurs in iron-black, very brilliant microscopic octahedra, with a submetallic lustre. They are not magnetic. They are insoluble in hydrochloric or nitric acid, but readily dissolve by fusion with bisulphate of potash. The quantity obtained was too small for further examination; but judging from analogy, there is no doubt as to its composition. It contains no nickel. By the decomposition of the above-mentioned salt, I have often obtained metallic cobalt, but never before this oxide. I will mention here, that I have several times observed the allotropic modification of oxide of nickel, in quantities not exceeding 0·5 or 1·0, in the metallic nickel manufactured in Hesse-Cassel, and imported to this country.—Silliman's *Journal*, January 1853.

Chemical Examination of the Food of the Queen Bee.
By Charles M. Wetherill, Ph.D.†

A specimen was given to me by Dr. Leidy, from Mr. Langstroth, of the food of the queen bee. It was an oblong mass, consisting of two differently-coloured layers, the inner one horn-like and transparent, the outer whitish and more opake. Under the microscope, with high powers, it appears amorphous. It was heavier than water, of the consistency of wax, but sticky and elastic. It contains wax, which is in larger quantity in the white than in the inner layer. Heated on the platinum foil, a portion of the body melts, and flows to another part of the platinum, where by further heating it diffuses the odour of wax. The residue does not melt, but swells up by greater heat, with a smell of burned leather, and leaves a porous coke, burning off with great difficulty, and with a slight ash. The substance in warm water is softened and partly dissolves, leaving white insoluble flakes; the filtrate gives a precipitate on boiling,

* Ann. der Chem. und Pharm., vol. liii. p. 139.
† Communicated by the Author.

which precipitate does not melt by heat, nor is it soluble in alcohol or æther. The original substance does not dissolve in alcohol or æther, but in the latter menstruum is covered on the surface with a white coating. In warm dilute hydrochloric acid it is slightly attacked, but not completely dissolved. Tested for nitrogen by Lassaigne's method, by fusion with sodium and obtaining the precipitate of prussian blue, it indicated the presence of considerable quantities of that element. As the body appears to be composed of at least three substances, and the quantity at my disposal weighed but 3 decigrms., I was unable to subject it to an ultimate analysis.

From its reactions it appears to contain, besides wax, albumen and proteine compounds. It is truly a bread containing albuminous compounds, which would probably prove on analysis similar to the gluten of wheat, for the nourishment of the plastic organs of the body. The examination of this substance was interesting in connexion with the Mexican ant-honey. The latter contains no nitrogen, and would therefore seem incapable alone of affording nourishment to the young insect, as supposed by some, and which young, in the case of bees, are fed by pollen. Perhaps the accumulation of honey in the ant is the result of a disease like diabetes, though it would seem improbable that it should be a disease so widely diffused.

The examination of compounds occurring in the lower animals, which are also the result of the decomposition of amylaceous and albuminous substances, and a comparison of these compounds with the animal's food, has been much neglected by chemists. Yet it would seem that the study of certain decompositions deemed physiologically important could be more readily carried out upon those lower orders, whose organs are less complex. The food of animals is in general very similar, as well in the per-centage proportion of its constituents as in the rational formulæ of its elements. It consists, as is well known, of nitrogenized compounds for formation, and amylaceous ones for respiration. The amylaceous compounds, in particular, have been well studied in all their transformations out of the body, and to a certain extent as occurring in man and in a few animals. The three principal radicals of this class, amyle, æthyle and formyle, and their compounds and derivatives, are well known. It is therefore significant, and suggestive of further research, when we find the three acids of their alcohol radicals in the animal, as valerianic in the oil of *Delphinus globiceps*, acetic in man, &c., and formic in the ant; these acids and other products of decomposition of the three radicals being besides found in other animals and in plants, and some in a diseased state of plant or animal. If it be desirable to study that mysterious force, the vital, how can it be done but by its effects, for which nature must be cross-examined in her every form? This is the more important, as we find vitality to determine the resolution of the same food into different products in different animals, as may be required for their existence. We have a beautiful example of this in the case of the

bee. One of the simplest transformations of an organic compound is that of cane- to grape-sugar; it requires merely the absorption of 2 equivs. of water by the former. Grape-sugar appears by the phænomena of fermentation to be more readily decomposable than cane-sugar; and we accordingly find this change taking place in the body of the bee in the formation of its honey, which is to be worked up again into wax. When cane-sugar is given to bees for the formation of wax, wax is indeed formed, but apparently with more difficulty, and does not detach itself readily, as in wax from honey. This excrement of honey, compared with food, is probably the simplest occurring in animal life.

The relation of food to respiration and nourishment in man and kindred animals has been well set forth by Liebig in his 'Animal Chemistry.' According to this author, an equivalent of starch is changed into fat by losing 1 equiv. of carbonic acid and 7 equivs. of oxygen. Now since wax bears a great analogy to the fats, it may be supposed to be derived from honey in a similar manner. Wax composed of cerine and myricine has a composition of $C^{34}\,H^{34}\,O^{2}$; anhydrous grape-sugar, $C^{12}\,H^{12}\,O^{12}$, or 3 equivs. $=C^{36}\,H^{36}\,O^{36}$: 3 equivs. of grape-sugar would therefore yield 1 of wax, 2 of carbonic acid, 2 of water, and 28 oxygen. That wax is produced from honey is shown by Grundlach (Natural History of Bees), as quoted by Liebig. The air in the hive during the formation of wax should contain an excess of oxygen, which has not been shown by analysis that I am aware of.

Grundlach supposes that honey is alone necessary to the support of bees without nitrogenized substances like pollen, and instances the fact that bees often starve in April when their honey is consumed, and when they can obtain pollen from the fields but no honey. But this perhaps only proves that much honey is necessary to their existence, owing no doubt to the large expenditure in the formation of wax, and which is not voluntary but continually going on; for the same author has observed, that bees shut up and fed without a queen will not build up honey-comb, although the wax laminæ will continue to be secreted from their bodies. If there is any analogy between bees and the Vertebrata, that nitrogenized compounds are as necessary to the formation of the plastic organs as the non-nitrogenized are to the respiration (and it would seem thus probable from the fact, that the queen bee, the fruit of whose labour requires much nitrogen, lives on highly nitrogenized food), it seems as incredible that bees should be supported entirely by honey as that man should be by starch only.

A careful examination of the relation between food and its transformation in the bodies of such animals would no doubt throw great light upon mooted points in physiology; and the many differences in the nature of the products, which could no doubt be reconciled with the laws of chemistry, would in themselves afford one of the strongest proofs in favour of the theories with which they might agree.

New Double Salts of Æthylamine and Propylamine.* *By* M. Reckenschuss.

Muriate of Æthylamine and Chloride of Palladium, $C^4 H^7 N$, $HCl + PdCl$.—If a watery solution of muriate of æthylamine be evaporated on the water-bath with an excess of a solution of chloride of palladium, a double salt crystallizes in black crystals, which are grouped in a feather-like manner, and appear of a fine red colour by transmitted light. They give a reddish-brown powder, and retain their lustre in the heat of the water-bath. The analysis of the crystals, dried at 212° F., gave—

Carbon	..	4 =	24·0	14·10
Hydrogen	..	8	8·0	4·71
Nitrogen	..	1	14·0	8·22
Palladium	31·26	1	53·2	31·25
Chlorine.....	..	2	71·0	41·73

Muriate of Propylamine also forms a beautifully-crystallized double salt with chloride of palladium, which when dry has an odour of herrings, and melts at 212° F.

Propylaminic Alum, $C^6 H^9 N, SO^3 + Al^2 O^3, 3SO^3 + 24HO$.—Sulphate of propylamine, prepared by the distillation of herring-brine, was mixed with a watery solution of sulphate of alumina, and left standing a considerable time in the air. Large crystals were obtained resembling common alum in appearance. These crystals are colourless and perfectly transparent; they emit a penetrating odour of herrings, dissolve in water, possess a sweetish astringent taste, fuse at 212° F., and at a temperature above 248° F. swell up remarkably, with loss of their water of crystallization. Analysis gave—

	Found.	Calculated.
Water	44·83	44·407
Sulphuric acid	32·38	32·89

These quantities consequently agree with the proportions calculated from the above formula.—*Ann. der Chem. und Pharm.*, lxxxiii. p. 343.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Remarks on the Structural Conditions of Iron. *By* T. R. v. Fuchs.

The difference in physical characters presented by the several kinds of iron is generally attributed to the presence of a variety of substances, among which carbon is considered the most important. It is contained in all kinds of iron, almost always accompanied by

* With regard to the propylamine with which the author operated, it may be stated, that, according to Hofmann's investigations (see Chem. Gaz., vol. x. p. 296), this is not propylamine, but the isomeric trimethylamine.—Ed. of *Chem. Pharm. Cent. Blatt.*

silicium, which perhaps exercises the same influence. Raw iron contains the largest quantity of carbon, bar iron the least, and steel is in some sort intermediate between the two; but the quantity of carbon does not in any case bear a constant proportion to the iron, nor are these three kinds of iron separated from each other by any definite limits. These two facts are sufficient to show that the carbon cannot be in a state of very intimate combination with the iron, and there are no sufficient grounds for assuming that the different conditions of this metal are determined solely by the quantities of carbon contained in it. The numerous, and in many respects valuable analyses of iron have served only to prove the truth of the above remark. Upon the gratuitous assumption that the varying per-centage of carbon is the cause of the differences in character of iron, attention has been too exclusively devoted to this point, while another, and perhaps more essential one, the crystalline structure, has been overlooked.

Fuchs expresses his conviction that iron is a dimorphous substance, that there are, in fact, two species (varieties) of iron,—the tesseral and the rhombohedral. He considers it as proved that malleable iron belongs to the tesseral system; and if any doubt still exists, it may be inferred from analogy that such is the case, inasmuch as all other malleable metals possess crystalline forms belonging to this system.

The crystalline form of raw iron has not been ascertained with so much certainty, but Fuchs considers it highly probable that it belongs to the rhombohedral system, because it comes within the class of perfectly brittle metals, the crystalline forms of which, as far as we are acquainted with them, are rhombohedral.

But the difference between malleable and cast iron does not consist merely in the crystalline structure, which may be open to doubt, but likewise in the physical characters, and to some extent in the chemical behaviour, for instance the cohesion, hardness, resistance to fracture, fusibility, oxidizability, solubility in acids, &c. He is of opinion that these circumstances alone would justify the inference that there is a specific difference between malleable and cast iron, which he compares with those presented by the modifications of sulphur, phosphorus, arsenious acid, by glass and Reaumur's porcelain.

Finally, with regard to steel, Fuchs is of opinion that it is an alloy of tesseral and rhombohedral iron. The per-centage of carbon which it contains varies from 0·625 (Gay-Lussac) to 1·9 (Karsten). It cannot therefore be regarded as a definite and constant compound. It differs from other alloys in the circumstance that its characters may suffer considerable alteration without an accompanying addition or loss of substance, as in the hardening and softening of steel, changes which Fuchs supposes to be the result of an internal and alternating metamorphosis, by which the relative proportion of the two species of iron is altered. Thus, according to his views, in hardened steel the rhombohedral preponderates over the tesseral iron, and the reverse in soft steel. Very hard steel would, therefore,

from the very small proportion of tesseral iron, approximate closely to cast iron; and this conjecture is favoured by the low specific gravity of hardened steel. By the process of tempering, the proportion of tesseral iron in steel would increase with the temperature. The two kinds of iron in steel may be regarded as in a state of constant mutual tension, which may perhaps be the reason why steel retains permanently communicated magnetism, while malleable iron does not.

An experiment of Schafhäutl's* would appear to favour the above views. He submitted a piece of a razor-blade to the action of tolerably strong hydrochloric acid for several days, at the end of which time it was found to have been very unequally attacked. When washed, dried and broken in a mortar, it furnished fragments, some of which could be powdered, while others were malleable.

With regard to the important and much-discussed question of the alteration of malleable iron when exposed to continuous vibration, concussion or torsion, in consequence of which it acquires a granular fracture, Fuchs admits that such an alteration takes place even in the best-worked metal, but does not altogether agree with the explanation usually offered for it, viz. the gradual assumption of a crystalline texture; and is of opinion that it consists in the passage of the iron from a fibrous crystalline state to a granular crystalline state, a change in the aggregation, not an essential metamorphosis. When iron passes from the fibrous into the granular texture, the cohesion of the molecules is lessened; and by their aggregation into rounded groups, a heap of distinct particles is produced, which may be compared with what mineralogists call granular minerals. The continuity of the mass is thus to some extent destroyed, inasmuch as these granular particles only adhere together more or less, and consequently the greater the size and number of these particles the greater is the diminution in tenacity. According to the statement of Kohn, the original condition of iron thus altered cannot be restored by heating to redness and forging, but only by exposure to a welding heat; and Fuchs considers this a sufficient proof that this alteration of iron consists in a breaking up of the continuity of the mass. The restoration of this continuity requires that the granular iron should, by exposure to a welding heat, be rendered amorphous, when the cohesive force again becomes active, a condition which in the case of most other bodies obtains only when they are liquid.—*Schweizerisches Gewerbeblatt*, September 1852.

New Methods for manufacturing pure Acetic Acid.

The decomposition of acetate of lime or lead by means of sulphuric acid has many inconveniences, and there is danger of the product being contaminated with sulphuric acid. Christl† was therefore induced to employ hydrochloric acid as a decomposing

* Prechtl's Technologischer Encyclopädie Abhandlung über den Stahl, vol. xv. p. 377.

† Dingler's Polytech. Journ.

agent, and has found that when this acid is not used in excess the distillate contains scarcely an appreciable trace of chlorine. A mixture of 100 lbs. of raw acetate of lime, obtained from the distillation of wood, and containing 90 per cent. of neutral acetate, with 120 lbs. of hydrochloric acid (20° Baumé), is allowed to stand during a night, and then distilled in a copper vessel. The application of heat requires to be gradual, in order to prevent the somewhat thick liquor from running over. The product of acetic acid amounted to 100 lbs. of 8° Baumé; it had a faint yellow colour and empyreumatic odour, which may be perfectly removed by treatment with wood-charcoal and subsequent rectification.

In order to obtain the acetate of lime sufficiently pure, Völckel* adopts the following process:—The raw pyroligneous acid is saturated with lime without previous distillation. A part of the resinous substances dissolved in the acid are thus separated in combination with lime. The solution of impure acetate of lime is either allowed to stand until it becomes clear or filtered†, then evaporated in an iron pan to about one half, and hydrochloric acid added until a drop of the cooled liquid distinctly reddens litmus-paper. The addition of acid serves to separate great part of the resin still held in solution, which collects together in the boiling liquid, and may be skimmed off, and likewise decomposes the compounds of lime with kreosote and some other imperfectly-known volatile substances, which are driven off by further evaporation. As these volatile substances have little or no action upon litmus-paper, its being reddened by the liquor is a sign that not only are the lime compounds of these substances decomposed, but also a small quantity of acetate of lime. The quantity of acid necessary for this purpose varies, and depends upon the nature of the pyroligneous acid, which is again dependent upon the quantity of water in the wood from which it is obtained. 150 litres of wood-liquor require from 4 to 6 lbs. of hydrochloric acid.

The solution of acetate of lime is evaporated to dryness, and a tolerably strong heat applied at last, in order to remove all volatile substances. Both operations may be performed in the same iron pans; but when the quantity of salt is large, the latter may be more advantageously effected upon cast iron plates. The drying of the salt requires very great care, for the empyreumatic substances adhere very strongly to the acetate of lime, as well as to the compound of resin and acetic acid mixed with it, and when not perfectly separated, pass over with the acetic acid in the subsequent distillation with an acid communicating to it a disagreeable odour. The drying must therefore be continued until upon cooling the acetate does not smell at all, or but very slightly. It then has a dirty brown colour. The acetic acid is obtained by distillation with hydrochloric acid in a still with a copper head and leaden condenser; when proper precautions are taken, the acetic acid does not contain a trace of either metal. The quantity of hydrochloric acid required cannot

* Ann. der Chem. und Pharm.

† A part is distilled off in a copper still in order to obtain wood-spirit.

be exactly stated, because the acetate of lime is mixed with resin, and already formed chloride of calcium. In most instances 90 or 95 parts by weight of acid, 1·16 spec. grav., are sufficient to decompose completely 100 parts of the salt, without introducing much hydrochloric acid into the distillate.

The distilled acetic acid possesses only a very faint empyreumatic odour, very different from that of the raw pyroligneous acid; it is perfectly colourless, and should only become slightly turbid on the addition of nitrate of silver. If the acid has a yellowish colour, this is owing to resin having been spirted over in the distillation. It is therefore advisable to remove the resin which is separated on the addition of hydrochloric acid, and floats upon the surface of the liquid, either by skimming or filtration through a linen cloth. The distilled acid has a specific gravity ranging between 1·058 and 1·061, containing upwards of 40 per cent. of anhydrous acetic acid. It is rarely that acid of this strength is required; and as the distillation is easier when the mixture is less concentrated, water may be added before or towards the end of the distillation. Völckel recommends as convenient proportions—

100 parts acetate of lime,
90 to 95 hydrochloric acid,
25 parts water,

which yield from 95 to 100 parts of acetic acid of 1·105 spec. grav. 150 litres of raw pyroligneous acid yield about 60 lbs. of acetic acid of the above specific gravity.

The acid prepared in this way may be still further purified by adding a small quantity of carbonate of soda and redistilling; it is thus rendered quite free from chlorine, and any remaining trace of colour is likewise removed. The slight empyreumatic smell may be removed by distilling the acid with about 2 or 3 per cent. of acid chromate of potash. Oxide of manganese is less efficacious as a purifying agent.

Although pure acetic acid may be procured by the distillation of vinegar, the whole of the acid cannot be obtained except by distilling to dryness, by which means the extractive substances are burnt, and the distillate rendered impure. In order to obviate this difficulty, Stein* proposes to add 30 lbs. of salt to every 100 lbs. of vinegar; the boiling-point is thus raised, and the acid passes over completely.

On the Fabrication of Oil of Roses in the Balkan.

It is principally the Christian inhabitants of the low countries of the Balkan between Selimno and Carloya as far as Philippopolis, who occupy themselves with the culture of the *Rosa centifolia provincialis*. In good seasons about 400,000 meticals (1 metical= 1½ drachm) are obtained in this tract of country. 400 roses form about 1 oka, 8 okas furnish about 1 metical of oil. In bad seasons

* Polytech. Centralblatt, 1852, p. 395.

only from 100,000 to 200,000 meticals of oil are obtained. The process followed, contrary to so many statements, is simply a distillation of the roses with water; this is performed in copper retorts, which contain about 30 okas of water and the same quantity of roses. The oil obtained varies in its properties; many Kasas? furnish an oil which solidifies more readily than others. The former is more sought after in commerce, but the more fluid oil has the finer odour. The oil is put into copper vessels, called "kunkunnas," which contain 100–1000 meticals; these, when filled, are soldered up. The rose-water which is obtained at the same time serves as a cosmetic, &c. The transit of the oil of roses is from Kasanlik through Constantinople.—Dingler's *Polyt. Journ.*, cxxvi. p. 78.

On the Detection of Cotton in Unbleached Linen.
By O. Zimmermann.

A piece of the stuff to be examined is well washed with boiling water and dried, then laid in a mixture of 2 parts of dried nitrate of potash and 3 parts of ordinary sulphuric acid, and left in intimate contact with it for 8–10 minutes according to the strength of the fabric. After a complete washing and drying, the piece of stuff which has been changed by the nitric acid is decocted with æther, to which some alcohol is added; the more consistent the collodion thus obtained, the more cotton was there in the linen. If no cotton be in it, the ætherial decoction is scarcely thickened. If it is wished to determine the quantity of cotton, it is only necessary to weigh the linen after it has been boiled with water and dried, then to proceed as above, separate the collodion obtained from the residue (which is unchanged linen), wash this well with some æther and alcohol, dry and weigh it; the loss of weight gives the quantity of cotton with tolerable accuracy.—*Archiv der Pharm.*, cxxii. p. 103.

PROCEEDINGS OF SOCIETIES.

Royal Society.

December 16, 1852.

On the Solution of Urinary Calculi in dilute Saline Fluids, at the temperature of the body, by the aid of Electricity. By H. Bence Jones, M.D., F.R.S., Physician to St. George's Hospital.

In 1848 the author first attempted to dissolve calculi in a solution of nitrate of potash, by placing them at the same time between the electrodes of a galvanic battery; an effect was produced on the uric acid at the negative pole, but no very decided result was obtained. The experiments were resumed during the last summer.

The results with uric acid calculi may be thus arranged. The action was chiefly at the negative electrode.

Experiments.	Duration of experiment. h m	Strength and temperature of solution.		Power of Battery.		Result. grs.
1.	4	Saturated solution of nitre	212°	10 pair		0½ dissolved.
2.	6 5	½ nitre, ½ water	109	5		11
3.	6 10	„ „	101	10		14
4.	6 20	„ „	100	10		16
5.	6 45	„ „	106	10		12
6.	3 17	„ „	98	20		27½
Oxalate of lime calculi were then tried.						
1.	7	½ nitre, ½ water	90	5		0½ dissolved.
2.	7	„ „	104	10		2
3.	6 15	In sulphate of soda	101	10		2
4.	5 45	In common salt	102	10		1
5.	6 10	½ nitre, ½ water	108	20		6
6.	3 19	½ nitre with phosphate of soda	110	20		1 dissolved.
7.	3 15	½ nitre with bichromate of potash	111	20		2
8.	3 17	½ nitre	110	20		2½
9.	2 50	½ nitre	92	20		2½
10.	3	„	100	40		5

Hence oxalate of lime calculi can be only very slowly dissolved in a solution of nitrate of potash, which acts far more energetically on uric acid calculi. The action is at least four times greater on uric acid calculi. Oxalates with urates, and oxalates with phosphates, were found to be far more rapidly acted on than oxalate of lime alone.

Phosphatic calculi were then taken. A piece of hard phosphate of lime gave

Experiments.	Duration of experiment. h m	Strength and temperature of solution.		Power of battery.		Result. grs.
1.	7½	½ nitre, ½ water	102°	10 pair		15
2. with fusible calculus	1 13	„ „	96	20		31

The action was chiefly at the positive electrode.

Experiments with marble.						
1.	5½	½ nitre	104	10		27½
2.	6½	In sulphate of soda	101	10		4½

From these experiments the following conclusions are drawn:— From two to nine grains of uric acid calculus can be dissolved in an hour in a neutral dilute solution of nitre at the temperature of the body, whilst in the same time from two to twenty-five grains of phosphatic calculus can be dissolved. However, only from half a grain to two grains of oxalate of lime can be removed by the same means in the same time. Still, if the stone consists of oxalate with urate, from one to two grains may be dissolved in an hour; and if it consists of oxalate with phosphate, from four and a half to five and a half grains can be taken away in that time.

These results may be obtained with calculi which have been long removed from the bladder, and have been dried at 212°.

MM. Prevost and Dumas in 1823 proposed to treat calculi by the galvanic pile. By means of the *mechanical action* of the mixed gases evolved by decomposing water, they found that phosphatic calculi might be disintegrated. The *chemical action* of the substances evolved by galvanic action on the surface of calculi was not determined by them.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Stannæthyle. *By* Prof. C. Löwig.

The investigations which the author has made and had made in his laboratory, as to the action of the iodides of æthyle, methyle, &c. upon alloys of antimony, arsenic, and bismuth with potassium*, have shown that these metals unite with æthyle, methyle, and amyle in the same proportions as with hydrogen, and form compounds which agree in chemical characters and constitution with ammonia and ammonium. It became therefore interesting to ascertain how metals not belonging to the antimony group would behave with the above radicals, and with this view alloys of tin and lead with sodium were subjected to the action of iodide of æthyle. In the present memoir the author communicates the results at which he has arrived with reference to the reaction of iodide of æthyle upon the alloy of tin and sodium. Although the investigation of stibæthyle, stibmethyle, &c. was accompanied by difficulties arising principally from the readiness with which these substances are oxidized, the investigation was nevertheless so far facilitated, that in the action of iodide of æthyle, iodide of methyle, &c. upon alloys of antimony and bismuth with potassium, only *one* compound is formed, and the alloys are readily and cheaply prepared by igniting these metals with tartar. By the reaction of iodide of æthyle upon the alloy of tin and sodium, on the other hand, there results at the same time an entire series of radicals, and compounds of them with iodine, the separation of which could only be effected after numerous analytical investigations; and, besides, no method of obtaining an alloy of tin with potassium or sodium has yet been discovered, except that of the direct combination of the metals. All attempts to obtain an alloy by heating tin or its oxides with tartar or other organic salts of potash, gave negative results. According to the proportions of tin and sodium in the alloy, or the quantity of quartz-sand added to it to moderate the powerful action of the iodide of æthyle, and according as the alloy or the iodide of æthyle are in excess, other combinations result; and it was only when the proportions were carefully attended to, which of course could not be foreseen at the commencement of the investigation, that the compounds attained a more simple and

* Chem. Gaz., vol. viii. pp. 201, 372, 395, 420.

determinate form, and it became possible to bring into unison the apparently isolated facts.

In the preparation of the compounds which tin forms with æthyle, the alloy of tin and potassium may be submitted to the action of iodide of æthyle, as well as the alloy of tin and sodium. At the commencement of the investigation the alloy of tin and potassium was employed; nevertheless the sodium alloy has several advantages; it is much more brittle, and therefore more readily pulverizable than that of potassium; it does not ignite during trituration, which is always the case with the latter, and further, sodium unites with tin more readily than potassium. The preparation of the alloy of tin and sodium presents scarcely any difficulties; the tin is melted by a moderate fire in a common earthen crucible, and the sodium, still moist with the naphtha, added to it in small quantities; during this, as a matter of course, the air must be excluded as much as possible, in which the adherent naphtha, which kindles immediately, assists greatly. When the sodium is melted, the whole is stirred with an iron rod, by which means the sodium is taken up by the tin immediately, and without ignition. When the sodium is completely incorporated, the crucible and furnace are closed, and the mass allowed to cool slowly. The operation must be quickly performed; in a quarter of an hour 2 or 3 lbs. of the alloy can readily be prepared. If 1 part of sodium be employed with 3 to 4 parts of tin, but not more, a strong expansion takes place at the moment of solidification of the mass, by which the crucible is always cracked; with 1 part of sodium and 6 parts of tin this expansion was not observed. The alloy is perfectly crystalline, of a silver-white colour, and may be long preserved, without apparent change, when kept in large pieces and covered with quartz-sand in a well-stopped bottle.

For the performance of the operation, small glass retorts of 3 to 4 oz. are employed. Into each retort is introduced an intimate mixture of about 2 oz. of the alloy with from 1 to 1½ part of quartz-sand. The alloy is to be quickly reduced to a fine powder in an iron mortar, and the sand added in small quantities. In two minutes at the utmost the retort must be filled with the mixture. This must then be instantly mixed intimately by shaking with such a quantity of iodide of æthyle that the whole may form a thick paste; the distillation-tube must then be quickly attached. In a few minutes the action commences, accompanied by considerable heat; it is more or less violent in proportion as the alloy contains more or less sodium. When the excess of iodide of æthyle has distilled off, the retort is closed air-tight whilst still warm, and the same operation repeated with a second retort. When two persons are at work, the operation may be repeated sixteen times in an hour; for this 1 lb. of iodide of æthyle is necessary. When the contents of the retort are perfectly cold, the mass is again moistened with iodide of æthyle. In from five to eight minutes, especially when the alloy employed consists of 1 part of sodium and 4 parts of tin, a strong reaction generally takes place. If, after being again cooled, a small quantity of the contents of the retort produces evolution of hydrogen

gas when put into water, iodide of æthyle must be added for the third time. The reaction which takes place is always accompanied by the development of so much heat, that the excess of iodide of æthyle is distilled off. On cooling, the mass in the retort is perfectly dry and powdery; it possesses a yellow colour and an intolerable odour. The contents of the retorts are now introduced into a flask which is nearly filled with æther, leaving only so much room that the whole can be shaken up. For sixteen retorts $4\frac{1}{2}$ to 5 lbs. of æther are required. The flask is then lightly closed, and the æther left for one or two hours in contact with the mass, with frequent shaking. The dark yellowish-brown solution is then decanted clear into a flask filled with carbonic acid, and left there from half an hour to an hour. During this time, especially if the air was not completely removed from the flask, a brown substance separates, which, when collected on a filter, dries in the air into a white inodorous mass. In the ætherial solution there are now five or six organic radicals and a number of iodine compounds; the latter are present in greater quantity when the contents of the retorts contain no undecomposed alloy; in the opposite case, and when the alloy consists of 1 part of sodium and 6 parts of tin, in general only the radicals are formed.

In the following statements it is to be understood that the author employed a mixture composed of 1 part of sodium and 6 parts of tin, and that both the radicals and the iodine compounds were dissolved in the æther. The radicals are insoluble, or soluble with difficulty even in absolute alcohol, whilst the iodine compounds are readily taken up even by hydrated alcohol. From a solution of nitrate of silver mixed with alcohol, the radicals immediately throw down metallic silver in the form of a black powder; the iodine compounds, on the contrary, instantaneously produce a precipitate of iodide of silver. At ordinary temperatures the radicals appear of the consistence of turpentine or olive-oil; they are completely insoluble in water, and are not moistened by it. Their odour is not very conspicuous, but difficult to characterize; it slightly reminds one of decaying fruit; if a drop be rubbed between the fingers, the odour of tin becomes remarkably distinct. The taste is unpleasantly acrid and burning. They neither catch fire nor fume in the air; but when ignited, they burn with a strongly luminous flame, and diffuse a thick white smoke of oxide of tin with sparks. If the ætherial solution of the radicals be allowed to evaporate spontaneously in the air, a gradual oxidation takes place, and the oxides of the radicals are obtained. These oxides remain either in the form of white amorphous powder, insoluble in water, alcohol and æther, or as a syrupy mass, which crystallizes after some time, and dissolves with difficulty in water, but readily in alcohol and æther. In this respect the radicals split into two distinctly separate classes. The oxides, which are insoluble in alcohol, are precipitated by ammonia from their saline combinations; those which are soluble in alcohol, on the other hand, separate the ammonia, are strong bases in every respect, and turn reddened litmus-paper blue like the alka-

lies. The radicals of the first class furnish with acids salts, which crystallize generally, and so also do the haloid compounds; they are nearly inodorous, whilst the haloids of the second class appear fluid and possess an odour like that of oil of mustard, which is exceeded in intensity by but few substances. All the radicals kindle with an explosion when a few drops of fuming nitric acid are added to them; dilute acid acts upon them as upon metals, the nitrate being formed with evolution of nitrous oxide gas. With halogens the radicals unite with the greatest violence, which in the case of bromine and chlorine is so intense as to produce ignition; they decompose the hydrogen acids, with evolution of hydrogen gas and the formation of haloids. From these properties it follows, that these radicals behave exactly like positive metals, and that each individual one, like a metal, is the source of a number of compounds. The object of the following investigation is merely to determine the nature of the radicals and their composition; and only so many of their compounds will therefore be described as may appear necessary for their characterization.

With regard to the elementary analysis, the author mentions that the determination of the carbon and hydrogen was performed with oxide of copper with which a little chlorate of potash was mixed. The anterior portion of the long combustion-tube was occupied by copper shavings, which took up the excess of oxygen completely. The determination of the tin presented difficulties. It is as intimately combined with the radicals as the carbon. Whilst on heating stibæthyle, bismuth-æthyle, and the allied substances, the metal is completely separated, the stannic radicals, when heated to redness, form a number of volatile products containing tin, which require particular study, and of which the author does not treat in the present memoir. Although nitric acid acts violently upon the radicals, the employment of strong acid produces a complete solution without separation of oxide of tin. If the solution be evaporated, and the residue carefully heated to redness in a covered platinum crucible, the quantity of oxide of tin obtained is 3 to 4 per cent., and even more than this, less than is required to correspond with the quantity of tin contained in the compound. It is only when the residue is again treated with concentrated acid and the solution evaporated, and this process repeated eight or nine times, that tolerably good results are obtained,—that is, when the nitric acid compounds are not volatile, which is the case with some of them. Several determinations of the tin were made in this manner. Nitromuriatic acid cannot be employed, on account of the volatility of the chloride of tin. The best results are obtained when the compound is burnt in a combustion-tube with oxide of copper, but without addition of chlorate of potash, and the residue in the tube treated with nitric acid, in which the oxide of tin then remains. The compounds of the radicals behave so exactly like inorganic salts, that their analyses present no further difficulties. In the determination of the iodine, it is advisable, after precipitation with nitrate of silver, to add a little more nitric acid.

Examination of the Substances formed by the Action of Iodide of Æthyle upon the Alloy of Tin and Sodium.

The ætherial solution of the radicals and iodine compounds formed by the action of iodide of æthyle upon tin and sodium mixed with $\frac{1}{12}$th to $\frac{1}{10}$th of absolute alcohol, and the æther completely driven off on the water-bath, leaves at the bottom of the retort a dark red or nearly black mass, of the consistence of turpentine, from which the alcoholic solution is to be poured whilst still hot into a vessel filled with carbonic acid gas. After standing quiet for twenty-four hours, a considerable quantity of a yellow oil separates, from which the clear alcoholic fluid is decanted. Although the radicals are nearly insoluble in alcohol, when they come in contact with it in their separate form, yet the alcoholic liquor contains a considerable quantity of them. Water is now to be added to this by drops, by which means some nearly colourless oleaginous fluids are thrown down; these are best preserved separately under water in well-stopped vessels. The addition of water is to be continued until the liquid no longer gives a precipitate of metallic silver, but pure iodide of silver, with a solution of nitrate of silver to which alcohol is added. The precipitated oils are the radicals; the iodine compounds remain in solution.

Examination of the Radicals.—The investigation of the radicals divides itself into—

1. The examination of the dark-coloured turpentine-like mass, which separates on driving off the æther from the hot alcoholic solution.
2. The examination of the yellow-coloured oil, which is deposited from the cold alcoholic solution after standing twenty-four hours.
3. The examination of the oleaginous colourless fluids, which are precipitated from the alcoholic solution by water.

I. *Investigation of the dark-coloured Turpentine-like Mass.*—This mass is taken up in very small quantity even by boiling alcohol, and separates again completely on the cooling of the solution. If alcohol be added in small quantities to its dark red ætherial solution, a nearly black greasy mass separates, and in proportion as this separation takes place the solution becomes decolorized. This precipitated mass is the radical $Sn^6 Ae^4$; it gave the following results on analysis:—

Tin	19·45	6 =	354	75·32
Carbon	4·17	16	96	20·43
Hydrogen.....	..	20	20	4·25

If the ætherial solution be allowed to evaporate spontaneously in the air, the oxide of the preceding radical separates in the form of a white powder, which dries into a tenacious mass. This substance, dried at 212° F., gave the following results:—

Tin.....	..	..	..	6 =	354	74·06
Carbon	18·60	18·31	18·12	16	96	20·09
Hydrogen ..	4·20	4·18	4·33	20	20	4·51
Oxygen	..	..	..	1	8	1·34

It is stated above that a substance often separates from the ætherial solution, which dries into a tenacious mass. This is the same oxide as the preceding, as it gave on analysis 18·12 carbon and 4·33 of hydrogen. It was dissolved in muriatic acid diluted with alcohol, the solution shaken with water and æther, and the ætherial solution which separates evaporated. In this manner the chlorine compound was obtained in the form of a beautiful pearly salt. Analysis:—

Tin	..	..	6 =	354·0
Æthyle.....	..	..	4	116·0
Chlorine	7·36	7·20	1	35·5

These results lead to the formula $Sn^6 Ae^4$ for the radical, $(Sn^6 Ae^4)O$ for the oxide, and $(Sn^6 Ae^4)Cl$ for the chlorine compound.

A gray powder frequently separates from the originally clear ætherial solution; this is scarcely soluble in æther and alcohol, possesses a penetrating odour, and takes fire on being mixed with fuming sulphuric acid. The results of its analysis agree with the formula $Sn^6 Ae^4 I$:—

Tin	58·8	58·6	6 =	354	59·2
Carbon	15·5	..	16	96	16·0
Hydrogen.....	3·8	..	20	20	3·5
Iodine	21·1	..	1	127	21·3

If the decolorized ætherial solution, from which the dark-coloured radical has been separated by means of a little alcohol, is evaporated without contact of air, a nearly colourless, thick, oleaginous fluid of spec. grav. 1·654 remains. This is readily soluble in æther, and is gradually but not completely precipitated by a large addition of alcohol. This substance was separated in small portions by means of alcohol from its ætherial solution, and each portion heated under water in the chloride of calcium bath until the adhering alcohol was completely volatilized. The separate portions were dissolved in æther, alcohol added to the solutions until the substance began to separate, and then the quantity of metallic silver determined which was thrown down by them from a solution of nitrate of silver to which alcohol had also been added. From the quantity of silver the atomic weight obtained for the first portion =88·49, 88·00; for the second portion 90·00, 91·00; and for the third 93·00, 94·00.

The first portion gave on analysis 27·30 carbon and 5·89 hydrogen, and 26·96 carbon and 5·86 hydrogen.

The second portion gave 26·99 carbon and 6·00 hydrogen, and 28·07 carbon and 5·83 hydrogen.

The third gave 28·00 carbon and 5·83 hydrogen, and 27·00 carbon and 6·00 hydrogen. It moreover contained 66·89 p. c. of tin.

These results agree with the formula SnAe:—

Tin.....	1 =	59	67·03
Carbon	4	24	27·27
Hydrogen	5	5	6·08

This radical is called by the author *Stannæthyle*. Its iodine compound was also obtained by Cahours, by exposing iodide of æthyle with tin in a closed tube to a temperature of 320° to 356° F.

It has been already stated, that the entire quantity of the dissolved radical is not thrown down from the ætherial solution by alcohol. If iodine be added to the alcoholic and ætherial fluid separated from the precipitates, so long as its colour disappears, and the solution left to spontaneous evaporation, remarkably beautiful, shining, acicular crystals are obtained, together with a small quantity of an oily fluid of a penetrating smell. The crystals at first possess the same odour; but if they be allowed to lie some time in the air, this odour disappears entirely, from which it seems that it only arises from a trace of the oily substance. The analysis of these crystals gave the following results:—

Tin	26·79	1 =	59	27·48
Carbon	11·19	4	24	11·16
Hydrogen.....	2·72	5	5	2·32
Iodine	59·20	1	127	59·04

From these facts, it follows that the substance which separates immediately after the æther is driven off is essentially stannæthyle, mixed with the red-coloured radical $Sn^6 Ae^4$.

II. *Investigation of the yellow-coloured Oil which separates on the cooling of the Alcoholic Solution.*—This substance appears as a fatty greasy mass, and separates after some time into two layers (this separation however does not always take place, and indeed only when the alloy employed contains 1 part of sodium and 6 parts of tin). The lower stratum possesses a faint reddish colour; it is perfectly transparent, and is of the consistence of olive-oil. Its analysis gave 27·48 carbon and 6·05 hydrogen, also 27·54 carbon and 6·04 hydrogen. This substance was dissolved in æther, the solution saturated with iodine, and then left to spontaneous evaporation. At first a small quantity of crystals, which were rather difficult of solution in alcohol, separated; afterwards a fine crystallization of long needles was obtained mixed with the strong-smelling oily substance. The acicular crystals contained 59·03 iodine. This oily fluid is therefore principally stannæthyle coloured by a small quantity of the dark radical.

The upper layer has a greenish-yellow colour and the consistence of a thick oil. It was dissolved in æther, and the ætherial solution shaken with a concentrated solution of potash. There immediately collected at the bottom of the vessel a thick, slightly-coloured mass, to which a little æther still adhered, which was completely removed by heating on the water-bath. The ætherial solution, which floated upon the solution of potash, gave on evaporation a nearly colourless oily fluid.

The substance which separated had a spec. grav. of 1·623, and contained according to analysis 17·30 carbon and 4·60 hydrogen. Its ætherial solution was saturated with iodine, and the solution then evaporated on the water-bath. There remained an oily mass, which

on cooling solidified in a crystalline form. This crystalline substance contained 13·36 carbon, 3·20 hydrogen, and 50·0 iodine. This iodine compound was dissolved in alcohol, and the solution left to evaporate spontaneously. First of all a salt crystallized in beautiful acicular crystals, grouped in a stellate form; large acicular crystals were afterwards obtained, which even from their outer appearance might be recognized as iodide of stannæthyle, as was shown to be the case by analysis. This gave 59·2 iodine. The crystals in stellate groups were again crystallized from alcohol, and then submitted to analysis, when they gave—

Tin	52·66	4 =	236	52·44
Carbon	15·26	12	72	16·00
Hydrogen.....	3·30	15	15	3·33
Iodine	28·78	1	127	28·22

The formula of the radical, which forms the base of this iodine compound, is therefore $Sn^4 Ae^3$. The author calls it *acetstannæthyle.*

The nearly colourless oily fluid which remained after the evaporation of the ætherial solution had a spec. grav. of 1·580. 0·570 grm. of the substance gave 0·803 grm. silver =0·060 oxygen. With 100 parts of the substance there were united therefore 8·3 of oxygen. The analyses also gave 24·98 carbon and 5·70 hydrogen, and 25·43 carbon and 5·81 hydrogen. This substance was also dissolved in æther, and after saturation with iodine, the ætherial solution mixed with alcohol was slowly evaporated; at first a small quantity of iodide of acetstannæthyle was obtained, and afterwards, together with the strong-smelling oily fluid, a large quantity of iodide of stannæthyle. The oily mass which separated from the alcoholic solution on cooling was consequently essentially a mixture of stannæthyle and acetstannæthyle.

III. *Investigation of the Substances precipitated in small portions from the cold Alcoholic Solution by the addition of small quantities of Water.*—In proportion as water was added to the cold alcoholic solution, the precipitates became more fluid and volatile. That which was last separated was perfectly limpid, and had a spec. grav. of 1·372. From the different quantities of silver thrown down by the different portions from solution of nitrate of silver, it appeared that the atomic weight of the precipitates increased in proportion as they were later thrown down, as may be seen by the following *résumé*:—

100 parts of the substance of the first portion gave 70 silver; of the second portion, 64 silver; of the third portion, 55 silver; of the fourth, 44 silver; and of the fifth, 36 silver.

The elementary analysis of these portions led to the following results:—

	I.	II.	III.	IV.	V.
Carbon	27·45	28·08	30·90	34·72	34·22
Hydrogen ..	6·15	6·17	6·65	7·70	7·23

When the several portions were converted into iodine compounds,

and their alcoholic solutions left to evaporate spontaneously, it appeared that the first and second portions still consisted principally of stannæthyle; but some other crystalline iodine compounds were always obtained, besides iodide of stannæthyle. The third, and especially the fourth and fifth portions, on the contrary, left behind iodine compounds of the consistence of syrup, and of a most fearful odour, in which, after long standing, fine rhombic tablets were formed. These oily fluids always occur, although only in small quantities, with the substances already mentioned.

Examination of the Rhombic Crystals.—As the crystals are rather difficult of solution in cold alcohol, whilst the oily fluid is miscible with it in all proportions, a partial separation of the two substances may be effected by pouring cold alcohol over the whole mass, and then quickly decanting the solution from the crystals. These are then pressed between filter-paper, and recrystallized from æther. In a pure state they are nearly inodorous; but if only a trace of the oil is mixed with them, they evolve a most disagreeable smell, which only goes off after long exposure to the air. Their analysis gave—

Tin.....	49·22	49·22	49·22	4	= 236	49·27
Carbon	19·61	19·14	29·28	16	96	20·04
Hydrogen ..	4·32	4·28	4·52	20	20	4·15
Iodine.....	25·74	26·00	25·10	1	127	26·52

The formula of the radical is consequently $Sn^4 Ae^4$. The author calls it *elaylstannæthyle.*

Examination of the Fluid Substance containing Iodine.—As has already been observed, this substance is the cause of the strong odour like oil of mustard, which is immediately observed on adding iodine to the mixed radicals; and when the other iodine compounds are crystallized from the mixture, this remains behind. It is perfectly colourless, often tolerably fluid, but generally of the consistence of a thick syrup. Its specific gravity varies between 1·7 and 1·6. Even from these properties it is evident that the substance must be a mixture; and, in fact, it was always found to have a different composition every time it was prepared. The difference in the quantity of carbon is inconsiderable, but greater in that of the iodine. The greater the quantity of iodine, the thinner is the fluid. Analysis gave—

	I.	II.	III.	IV.
Carbon.....	23·18	23·51	24·25	22·48
Hydrogen....	5·60	5·16	5·30	5·28
Iodine	29·66	38·80	30·88	35·23

No doubt small quantities of iodide of stannæthyle, and of the crystallizable iodine compounds generally, are still dissolved in the fluid substance.

As these fluid iodine compounds are rather volatile, an attempt was made to effect their separation by distillation. The substance was not however submitted to distillation by itself, but with water; and the parts which went over at the commencement, at the middle, and at the end of the operation were collected separately. Each

portion was separated from the water, and dried with a few fragments of chloride of calcium. That which first went over, which was a rather thin fluid, gave the following results:—

	I.	II.	III.	IV.
Carbon.....	22·28	22·69	22·24	22·51
Hydrogen....	5·27	5·18	5·06	5·20
Iodine	..	35·00	30·00	27·44

From these analyses it appears with certainty, that the volatility decreases in proportion as the quantity of iodine diminishes. Admissible formulæ cannot however be calculated from them. As this method led to no result, the author prepared the oxides of the radicals. To each part dissolved in alcohol, freshly-precipitated oxide of silver, which had been washed in alcohol, was added until the smell had entirely disappeared. The alcoholic solution filtered from the iodide of silver had a strong alkaline reaction, and an exceedingly powerful, acrid, burning taste. After evaporation there remained of the volatile substance beautiful columnar crystals, mixed with a small quantity of tufted crystals, and of the thicker fluid, tufted crystals with which a small quantity of columnar crystals was mixed.

The oxides were dissolved in alcohol, then exactly saturated with sulphuric acid, and the solutions left to evaporate spontaneously. The oxide of the thick fluid gave first of all small lanceolate crystals, which immediately lost their transparency in the air; it afterwards furnished a small quantity of fine columnar crystals. The oxide of the thin fluid yielded remarkably beautiful, brilliant, large, columnar crystals, which did not change in the air, and with which only a small quantity of the lanceolate crystals was mixed. As the latter are more difficult of solution in alcohol, the two salts could be readily separated, and obtained perfectly pure by repeated crystallization. The salts were exposed to a temperature of 77° F. for some time, and then submitted to analysis. For the determination of the sulphuric acid the salt was dissolved in alcohol, and some muriatic acid added to the solution; chloride of barium was then added, and the whole put upon the water-bath, without filtering the fluid from the sulphate of baryta, and evaporated to dryness. After the organic chlorine compound had been volatilized, the residue was treated with water, and the sulphate of baryta collected on a filter. The combustion was performed with oxide of copper and a little chlorate of potash. The water obtained was perfectly pure, and contained no trace of sulphurous acid. The analysis of the columnar crystals gave—

Tin.....	..	..	..	..	2	=118	46·60
Carbon	28·01	28·17	28·43	28·02	12	72	28·45
Hydrogen	5·94	6·24	6·01	6·08	15	15	5·93
Oxygen.....	..	..	..	..	1	8	3·21
Sulphuric acid ..	15·79	15·56	15·78	15·72	1	40	15·81

The formula of the salt is therefore $(Sn^2\ Ae^3)O, SO^3$. The radi-

cal consequently consists of $Sn^2 Ae^3$; the author calls it *methylstannæthyle*, or, for brevity, *methstannæthyle*.

The analysis of the lanceolate crystals gave—

Tin	..	..	..	4	=236	55·03
Carbon	27·31	27·53	27·11	20	120	27·97
Hydrogen	6·01	5·98	5·75	25	25	5·82
Oxygen	..	..	..	1	8	1·86
Sulphuric acid	9·20	9·17	8·91	1	40	9·32

The formula of the salt is therefore $(Sn^4 Ae^5)O, SO^3$, and that of the radical $Sn^4 Ae^5$. This radical is called *æthylstannæthyle* or *æthstannæthyle* by the author.

If the analyses above given of the iodine compounds be compared with the composition of these sulphuric acid salts, it is evident that the former are mixtures of iodide of methstannæthyle with the iodide of æthstannæthyle:—

		$Sn^2 Ae^3 I$		and	$Sn^4 Ae^5 I$.	
Tin	2 =	118	35·64	4 =	236	46·46
Carbon	12	72	21·62	20	120	23·62
Hydrogen..	15	15	4·52	25	25	4·90
Iodine	1	127	38·22	1	127	25·02

From these investigations, it appears that at least six radicals are formed by the action of iodide of æthyle upon the alloy of tin and sodium, namely—

Stannæthyle.....	Sn Ae	Methstannæthyle ..	$Sn^2 Ae^3$
Elaylstannæthyle..	$Sn^4 Ae^4$	Æthstannæthyle ..	$Sn^4 Ae^5$
Acetstannæthyle ..	$Sn^4 Ae^3$	The radical	$Sn^6 Ae^4$.

To these must be added, as appears from what follows, a radical of the composition $Sn^2 Ae^2$.

Investigation of the Iodine Compounds which are formed simultaneously with the Radicals during the Action of Iodide of Æthyle upon the Alloy of Tin and Sodium.—As has already been stated, there are usually formed, simultaneously with the radicals, during the action of iodide of æthyle upon the alloy of tin and sodium, iodine compounds, the number and quantity of which vary, both according to the composition of the alloy of tin and sodium, and according as the alloy or the iodide of æthyle is in excess. Alloys of 1 part of sodium to 6 parts of tin, mixed with an equal quantity of sand, furnish, when employed in excess, only the radicals; whilst mixtures containing a larger quantity of sodium, with an excess of iodide of æthyle, always furnish iodine compounds also. In the latter case the action is uncommonly violent; and the evolution of heat is so great, that sometimes the mass becomes red-hot in particular spots, which of course must be avoided by an increase in the quantity of sand employed.

The iodine compounds formed may be divided into two groups. Those of the first group possess the faculty of crystallizing; in the pure state and after long exposure to the air they are nearly inodorous; those of the second group are fluid, generally of an oily

consistence, and possess an exceedingly powerful smell. The former are sometimes formed in such large quantities, that they partially separate in a crystalline form, when the æther is driven off from the alcoholic-ætherial mixture, and are mixed with the radicals. In this case their separation may be effected by cold alcohol, in which the iodine compounds are soluble. They generally however remain dissolved, and are then to be met with in the alcoholic fluid from which the radicals have been precipitated by gradual addition of water. If this is left to spontaneous evaporation, small hard crystals generally separate first, which are soluble with difficulty in alcohol, and crystallize from their boiling alcoholic solution in a tabular form. Afterwards there appears a plentiful crystallization of needles in stellate groups; and after the completion of the evaporation there remains a mass, sometimes of a thick, sometimes of a thin fluid consistence, and of a penetrating odour. If this residue is dissolved in alcohol, the solution shaken with æther, then with sufficient water to separate the æther, and the ætherial solution is evaporated, the oily residue deposits rhombic tables, which can only be separated with difficulty from the oily fluid, and not without considerable loss. Iodide of stannæthyle is still dissolved in the watery alcohol; this can be obtained in a crystalline form by evaporation. The analysis of the crystals which separate first from the alcoholic solution gave—

Tin	..	..	2 =	118	39·22
Carbon	15·13	14·84	8	48	15·84
Hydrogen ..	3·32	3·12	10	10	3·03
Iodine	41·25	41·25	2	127	41·91

The formula is consequently $(Sn^2 Ae^2)I$. The radical $Sn^2 Ae^2$ is called by the author *methylenstannæthyle.*

The analysis of the stellate crystals leads, as follows, to the composition of iodide of acetstannæthyle, $Sn^4 Ae^3 I$:—

Tin	51·64	51·64	51·64	4 =	236	52·45
Carbon	15·25	15·41	15·50	12	72	16·00
Hydrogen ..	3·46	3·41	3·45	15	15	3·33
Iodine	28·06	28·38	28·34	1	127	28·22

Analysis of the Rhombic Tables.—The crystals were separated from the oily fluid by pressure, dissolved in æther, and the ætherial solution left to evaporate spontaneously. They are iodide of elaylstannæthyle, $Sn^4 Ae^4 I$:—

Tin	49·27	..	..	4 =	236
Carbon.....	20·04	19·71	19·26	16	96
Hydrogen ..	4·15	4·40	4·22	20	20
Iodine	26·52	26·51	26·50	1	127

Analysis of the Oily Fluid.—The physical properties of this fluid, especially its penetrating odour, point at once to the fact that it is a mixture of the iodides of methstannæthyle and æthstannæthyle, as was also shown to be the case on analysis:—

1. The substance of spec. grav. 1·625 contained 23·78 carbon, 5·20 hydrogen, and 31·04 iodine.

2. The substance of spec. grav. 1·540 contained 23·48 carbon, 5·25 hydrogen, and 29·70 iodine.

3. The substance of spec. grav. 1·770 contained 23·31 carbon, 5·16 hydrogen, and 34·67 iodine.

From this investigation it follows that the iodine compounds are formed simultaneously with the radicals.

[To be continued.]

Note on the Existence of Boracic Acid in various natural Substances. *By* M. E. Filhol.

H. Rose having discovered some time since that a mixture of boracic acid with muriatic acid communicated a red colour to turmeric paper, showed by means of this reaction that the waters of Aix, in Savoy, contained a little boracic acid. M. Jules Bouis has subsequently proved that the sulphurous waters of Olette (Pyrénées-Orientales) also contain boracic acid.

I was engaged at the same time as M. Bouis in similar experiments, which I intended to have published in course of time; but the note of M. Bouis compels me to make known immediately the results which I have obtained.

I have discovered boracic acid in the sulphurous waters of Bagnères-de-Luchon, Barèges, Cauterets, Bonnes and Labarière. I have also ascertained the existence of this acid in the waters of Vichy, in which I believe it is more abundant than in the sulphurous thermal springs of the Pyrenees; this shows that the presence of boracic acid in waters is by no means connected with their issuing from a granitic soil. I have found traces of boracic acid in the felspars of the Pyrenees, and also in some pegmatites from the department of Aveyron.

Lastly, and this is not the least curious of the results which I have obtained, I have discovered the existence of boracic acid in several samples of commercial potash, and also in some carbonate of potash, which I prepared myself by the lixiviation of common ashes and evaporating the solution to dryness.

It appears to me therefore that boracic acid must very frequently, if not always, accompany silicic acid; that it is probable that it will be discovered in all alkaline waters which are rich in silica; and that the existence of traces of boracic acid in a spring is not sufficient to prove that this spring owes its origin to hidden volcanoes, as the acid may be found in the ashes of most vegetables, even when they have been grown in a situation very distant from any chain of mountains, and not presenting any traces of volcanic action.

The quantity of boracic acid contained in the waters of the Pyrenees, as far as I can judge from the experiments which I have made, is very small, and I do not think that any one could dream of extracting it from those which I have mentioned in this note. This by no means invalidates the results of the experiments of

M. Bouis, as the springs of the Eastern Pyrenees may be richer in borates than those of the rest of the chain, from which they differ, in my opinion, in other respects.

Of course the correctness of the preceding results is dependent upon that of the reaction indicated by Rose.—*Comptes Rendus*, Feb. 21, 1853, p. 327.

On the Preparation and Properties of Magnesium. By R. Bunsen.

According to Bunsen, fused chloride of magnesium is readily decomposed by the galvanic current. A metallic mass of several grammes in weight may be prepared in a short time with a few pairs of the carbo-zinc battery.

Magnesium obtained in this manner, when freshly broken, is sometimes slightly crystalline and laminar, sometimes finely granular, or even fibrous, according to the mode in which it is broken; in the former case it is silver-white and very shining, in the latter more bluish-gray and dull. Its hardness is less than that of calc-spar. A moderate red heat is sufficient to fuse it. In dry air it is completely unchanged, and does not lose even the lustre of its surface; but in moist air it is speedily covered with a layer of hydrate of magnesia. Heated to redness in contact with the air, it ignites, and burns with an intense dazzling white light, forming magnesia. The light evolved during combustion in oxygen is of unusual intensity. A piece weighing 0·1 grm., burnt in this gas, gave a light equal to that of about 110 wax candles. As the surface of the burning metal was but small, that of the effective portion of the candle-flame being six or eight times larger, it may be supposed that the intensity of the light of magnesium burning in oxygen gas exceeds that of a candle-flame more than 500 times.

The metal decomposes pure cold water but slowly; water containing acid, however, is rapidly decomposed by it. Thrown upon dilute nitric acid, it ignites instantaneously. Concentrated sulphuric acid dissolves it with difficulty. It is not attacked by a mixture of sulphuric acid and fuming nitric acid in the cold. It burns in chlorine gas when heated previously to its introduction, and also in vapour of bromine, but with more difficulty. Its combustion in the vapours of sulphur and iodine proceeds with greater liveliness. Its spec. grav. at 41° F. is 1·7430. If the atomic volume of magnesium be calculated from this, it is found to be twice that of nickel, namely 86 instead of 43. The magnesium obtained by electrolysis may be readily filed, bored, sawn, and beaten out flat, but exhibits scarcely more ductility than zinc at ordinary temperatures, whilst that reduced by potassium is very extensible, and may be hammered out into thin plates. This difference arises from the circumstance that the magnesium reduced by potassium retains a little of that metal; that obtained in the electro-chemical way, on the other hand, nearly always contains a small quantity of aluminium and silicium.

Barium, calcium, and strontium cannot be reduced in the same manner.—*Ann. der Chem. und Pharm.*, lxxxii. p. 137.

A Method of getting rid of Sal-ammoniac in Analysis.
By Dr. J. Lawrence Smith.

There is nothing in mineral analyses more embarrassing than the accumulation of sal-ammoniac towards the end of an analysis, especially where potash and soda are to be estimated. The only method now adopted to get rid of this ammoniacal salt is to volatilize it by heat, which, if the quantity be considerable, is attended with no little annoyance, and a certain loss of more or less of the fixed alkalies which may be present. I have within the last twelve months discovered a method of overcoming that difficulty, and much experience during that time has proved that it is of considerable value. The method is simply to add nitric acid to the solution containing the sal-ammoniac and alkalies, and heat it gently over a lamp or sand-bath in a glass flask or porcelain capsule. The nitric acid may be added either before the liquid is concentrated or after concentration; a most quiet decomposition ensues, and the liquid readily evaporates to dryness, leaving nothing but the fixed alkalies if they be present. I am in the habit of using a little more than 3 grms. of pure nitric acid of ordinary strength to every gramme of sal-ammoniac supposed to be present in the liquid. The exact nature of the decomposition which ensues cannot now be stated, but there is doubtless formed, besides other things, chlorine, hyponitric acid and nitrogen. I shall not enter more into detail about this method, as I intend doing this at a future time; only wishing at present to take precedence in what I presume to be a method of some importance in analytical chemistry, and never to have been used before for this purpose.—Silliman's *Journal*, January 1853.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Soaps, and their Employment in Manufactures.
By Prof. F. C. Calvert.

It may perhaps be desirable that, before I enter into the technical details contained in this paper, I should give a short outline of the manufacture of soaps, and of their chemical composition. The manufacture of soaps may be ranged under two great heads, the one relating to soft soaps, and the other to hard soaps. Both soaps contain fatty matter; but in the former case it is combined chiefly with potash, in the latter with soda. There is also another important difference between these two classes of soap, for soft soaps contain all the substances which composed the fatty matter employed in their preparation, whilst in the soda soaps one of these substances is removed, namely the oxide of glyceryle, or glycerine. Thus, in the manufacture of soft soaps, either the fatty matters mixed with a large proportion of fish-oil, or the fish-oil itself,

are boiled with caustic ley; and when saponification is effected, and the whole sufficiently concentrated, it is allowed to cool; whilst in the case of hard soaps the caustic leys employed contain a sufficient amount of water to dissolve the glycerine as it is removed from the fatty matters by the action of the alkali contained in the caustic ley. From these facts it may be seen that the chemical change which takes place consists in the substitution of oxide of potassium or sodium for the oxide of glyceryle existing in the fatty matters in the state of a margarate, stearate, or oleate, and therefore in the formation of a margarate, stearate, or oleate of potash or soda, soluble in water. It is easy to understand that a great variety of soaps must be manufactured to suit the various purposes to which soaps are applied in domestic and manufacturing concerns; and so we find that different qualities of soap are manufactured for boiling silks, clearing wool, or for clearing madder goods, and giving to the different colours obtained from this root a greater brilliancy and fixity. Strange to say, we are quite ignorant of the real composition which each of these soaps should present to produce the maximum of effect, and we are even unacquainted with the composition of those now employed. I have therefore thought that it might be interesting if I were to offer a statement of the results I have obtained in connexion with this point. To arrive at a medium, showing the real difference which exists between soaps employed for the above purposes, I have been obliged to make a great number of analyses. This will be easily understood if we reflect that the quality of the soaps used by different parties, in a given trade, is so little examined, that even the soap used by a single firm varies as much as 25 per cent. in quality. The following general results I have however arrived at in calculating the composition of these soaps as containing 30 per cent. of water:—

Composition of Soaps per 1000 *parts.*

	Calico printers' soap.	Silk dyers' soap.	Wool scourers' soap.
Fatty matters.....	640	619	614
Soda	60	81	86
Water.....	300	300	300

From these results we find that the soaps employed vary in the quantity of alkali according to the nature of their application; thus in 1000 parts of soap, there are 21 parts more alkali in the one used for boiling silk, and 26 parts more alkali in that employed for clearing wools, than there are in the soap best suited for clearing madder purples. These facts show us at once how important it is to inquire into the real composition of a soap before employing it for a given purpose. If, on the one hand, a calico printer were to use a soap which had the composition of the one used by the wool scourer, he would cause the shade of his madder purples to fade; and if, on the other hand, the wool scourer were to employ the neutral soap of the calico printer, he would have but imperfect results, owing to this circumstance, that in the latter case an excess of alkali

is essential, not that the alkali may combine with the fatty matters of the wool, but that it may form an emulsion with the stearine and elaine discovered by M. Chevreul, and thus liberate the dirt which they fix on the wool. There is another point which deserves the serious attention of calico printers, and that is, the influence which soaps of different compositions must have on the different shades obtained in madder dyeing; for it must be obvious that the soap containing a slight excess of alkali, which is the best suited for clearing madder reds or dark pinks, would deteriorate the beauty of the madder purples. In the first case, the dyer has in view, not only to fix and brighten his reds or pinks, but further to remove the yellow colouring matter, and also partially the red; whilst in the latter a soap containing as little alkali as possible appears to me to give the best results. I have found by experiment the two following soaps to be best suited for these purposes:—

	Soap for purples.	Soap for dark pinks.
Fatty matter	60·4	59·23
Soda	5·6	6·77
Water	34·0	34·00

Still we find that calico printers in general employ the same quality of soap for all shades of madder goods. Some dyers think that they overcome this difficulty by employing less or more of the same soap; but this is an error, not only as manifested by the above remarks, but because, as we shall show presently, the different soaps sold in the market offer in their relative composition differences which are equal to the different proportions they are in the habit of using for given styles or shades of madder prints. This fact can be easily proved by examining the qualities of soap which are supplied to a firm during a period of twelve months; for we find, as the following results show, that the quality of soap sometimes varies as much as 25 per cent. in value:—

	I.	II.	III.	IV.	V.
Water	26·00	29·3	34·81	38·0	45·00
Fatty matter	66·00	64·0	56·00	55·4	46·01
Alkalies	7·56	6·3	6·98	6·1	5·80
Impurities	0·43	0·4	2·21	0·5	2·19

The figures also show that the quantity of the really effective agent, viz. the fatty matter, in a soap may vary from 46 to 66 per cent.; consequently it may be seen that a large sum of money is wasted by some of our large firms annually, for want of paying proper attention to one single article. It must be remembered that each piece of madder-dyed goods requires from 1 oz. to 4 oz. of soap to clear it. If we take the average at 2 oz. per piece, and admit that a print-works produces 100,000 pieces per annum, the quantity of soap used would be 12,500 lbs.; and if the soap be 25 per cent. under value, the loss would equal 4125 lbs.

It may be objected that the above soap was supplied to one firm only, and therefore its variation in quality might be owing to the

inattention of persons connected with the firm. This remark would however have no value, as I have found similar differences of quality in the soap of other firms.

There is another fact connected with the use of soap by calico printers which deserves most serious consideration, and to which attention has not, so far as I am aware, been drawn, viz. that soaps are not at the present day, as formerly, made with one kind of fatty matter, but are manufactured sometimes from palm-oil, at other times with vegetable fluid oils, such as rape-seed oil, galipoli-oil, again with animal fatty matters, and lastly with the oily liquid called oleine, which is obtained when solid fatty matters are submitted to pressure to obtain a fatty matter having a higher fusing-point, and consequently more fit for the manufacture of composite candles. The liquid oleine, containing small amounts of margarine and stearine, is extensively employed at the present day in the manufacture of soaps. I have ascertained from direct experiment, that such a soap will not give the same brilliancy and fixity of colour to the shades obtained from madder roots as a soap made with a vegetable oil composed of margarine and oleine, or with an animal fatty matter composed of margarine, stearine and oleine; consequently if a dyer uses a soap of the former composition, it will prove, if not a direct loss to him, at least an injury to his goods, in disabling him from producing the maximum effect. I should also mention here, that I have found in print-works household soap of an inferior quality, and containing 10 per cent. and upwards of resins. These soaps have none of the properties required in calico printing, and must therefore prove a loss to the printer, as well as those soaps which are sometimes found to contain glue. I hope these facts will prove how highly desirable it is, that, with the existing competition both amongst our local firms and those of the continent, the indifference which exists as to the qualities of the drugs employed in print-works should cease, and that science united with practical knowledge should step in, and guide the application of chemical art in manufactures. Then, and then only, will our manufacturers progress in a sound and remunerative manner.

I have also examined a great variety of soaps employed for omestic purposes, and have found their qualities to vary materially, as the figures underneath show:—

	Hard soap.			Soft soap.	
	I.	II.	III.	I.	II.
Fatty matters, &c. ..	67·00	57·52	56·09	41·67	58·95
Water	26·81	36·00	39·14	49·49	32·15
Alkali	6·19	6·48	4·77	8·84	8·90

Manchester Guardian, Feb. 12, 1853.

On the Determination of Water in Commercial Iodine.
By M. Bolley.

Powdered iodine takes up a tolerably large quantity of water without experiencing any remarkable alteration in appearance. The

quantity of water thus mechanically mixed with iodine may, according to some authorities, amount to as much as 10 or 12 per cent., and the methods for determining it are very insufficient. Although less volatile than water, this substance, like many others, is very readily carried off by the vapour of water. Chevallier recommends that the quantity of water should be determined by pressing a known weight of the iodine between folds of bibulous paper, and then weighing it again. It is evident that this method cannot furnish accurate results. Another method consists in rubbing the iodine with twice its weight of fused chloride of calcium, and heating the mixture to 356° F. in a tubulated retort, by which means the iodine is volatilized, while the water is retained by the chloride of calcium. In this case care must be taken that water is not evaporated from the chloride, and there is considerable trouble in thoroughly removing the iodine from the neck of the retort.

Bolley proposes the following method as being both simple and accurate. About 30 grs. of iodine are introduced into a small porcelain dish previously weighed, about 240 grms. of mercury added, and the whole weighed together with a small agate pestle. The dish is then laid upon a sheet of white paper, and the iodine and mercury rubbed together by means of the agate pestle until the smell of iodine has disappeared and the mass has assumed a reddish-brown colour*. When complete combination has been effected, the dish is placed in a water-bath, and after some time weighed. The loss of weight gives the quantity of water in the iodine. There is a slight loss of water in this operation, in consequence of the heat developed during the combination of the iodine and mercury, but the quantity of iodine volatilized is very minute. It is advisable to lay a piece of starch-paper over the dish while in the water-bath, so as to be sure that no iodine has been lost in consequence of imperfect combination. The following results of the examination of three kinds of iodine will give some idea of the applicability of the process; two determinations were made in each case immediately after each other:—

Iodine A. I.	3·79 p. c.	B. I.	4·05 p. c.	C. I.	6·31 p. c.
II.	3·61 p. c.	II.	3·88 p. c.	II.	6·18 p. c.

Schweizerisches Gewerbeblatt, September 1852.

Fire-proof Bronze Colour for Copper and Brass. By M. Dienst.

$\frac{1}{16}$th of an ounce of crystallized verdigris, and the same quantity of finely pounded muriate of ammonia, are to be dissolved in $\frac{5}{6}$ths of a pint of rain-water, the solution left standing covered for 3 to 4 hours, and then $1\frac{1}{2}$ pint more water poured into it. The copper vessel,

* It suddenly becomes pasty, and closely resembles an amalgam, a fact which does not appear to have been noticed. To effect this, a quantity of mercury six or eight times as great as that of iodine appears necessary. The uncombined mercury may be pressed out from the iodine, which does not destroy the continuity of the former.

which must be perfectly clean, is now to be held over a charcoal fire until it is equally heated throughout and becomes uniformly tarnished. The copper is now to be rubbed over with the mixture, and then carefully dried.

After five or six repetitions of this treatment, the copper receives a brass colour; after from six to ten repetitions, it acquires a fine yellow. If the copper is now to be changed from yellow to brown, it must no more be wetted whilst hot; if, however, it be desired to have it very pale brown, the process must be repeated twenty or twenty-five times. When the desired colour is attained, the copper is to be laid in clean water, taking care however to clean it or dry it rapidly after taking it out. This must be done carefully. The copper is then held over a weak charcoal fire, when the bronze becomes permanent and fire-proof.

To give a fire-proof, brown, bronze colour to brass, the following is the process:—

$\frac{3}{32}$ of an ounce of crystallized verdigris and the same quantity of sal-ammoniac are mixed with $\frac{5}{6}$ths of a pint of rain-water, and left to stand for 2 to 3 hours. The brass is then to be rubbed over with it for 2 to 3 minutes, when it becomes green. $1\frac{1}{4}$ pint of rain-water is now to be added to the solution. The metal is now held over a charcoal fire, which must not be too strong, until it acquires a copper colour. It is then again wetted, and left to dry by evaporation. When it has been treated in this manner four or five times, it becomes olive-coloured. The heat may now be somewhat increased, but it is necessary to be very careful that the metal does not become too hot. When it has been treated nine or ten times in this manner, it becomes brown. As long as any greenish places are to be seen, however, this treatment must be continued, in many cases 20 to 25 times before the required colour is obtained.

If however the metal be strong, the materials are to be dissolved in hot rain-water, and the metal rubbed with it immediately until it acquires a fine dark green colour; it is then to be held over a strong charcoal fire, by which means it acquires a fine brown colour after 10 to 12 repetitions of the treatment. It is necessary to be careful that the metal is equally heated throughout. If spots appear, they must be bitten out during the work and polished with brick-dust.—*Gewerbeblatt aus Würtemb.*, 1852, No. l. p. 409.

Examination of Guano. By M. Melsens.

A solution of chloride of lime is prepared by extraction of chloride of lime with water; some hydrate of lime is added to the clear solution, which is then filtered. 1 grm. of guano enveloped in paper is then put into a bottle containing the above fluid, and the gas evolved collected. The value of the guano is determined by a comparison of the gases obtained with those procured from the best sorts of guano.—*Moniteur Industriel*, 1852, No. 1677.

THE CHEMICAL GAZETTE.

No. CCLI.—April 1, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Combinations of Glycerine with Acids. By M. Berthelot.

According to the researches of M. Chevreul on the fatty bodies, most of the substances examined by him were capable of being resolved by saponification into fatty acid and glycerine, with fixation of the elements of water. The analogy established by this fact between fatty substances and æthers was first pointed out by M. Chevreul.

M. Pelouze has attempted the inverse operation, that of reuniting glycerine with the acids, in the same manner as alcohol is combined with these substances. He has succeeded, on the one hand, in obtaining by direct union sulphoglycerates and phosphoglycerates analogous to the sulphovinates and phosphovinates*; on the other†, in combining glycerine with butyric acid, the most readily ætherizable of all the acids.

Butyrine, the only neutral fatty substance which has hitherto been reproduced, is obtained by indirect ætherification, by causing either sulphuric or hydrochloric acid to act upon a mixture of glycerine and butyric acid.

I have succeeded in combining glycerine with other acids, namely, the acetic, valerianic, benzoic and sebacic acids, and others. The process which furnished these compounds is, with some modifications, that which is employed to ætherize the fatty acids, and which furnished butyrine to MM. Pelouze and Gélis. I mix the dry acid with syrupy glycerine, heat the mixture to 212° F., pass through it a current of hydrochloric acid gas during several hours, keeping the mixture at that temperature, and then allow it to cool in the current of gas. I then leave the whole at the ordinary temperature for several hours, days, or even weeks, if necessary repeating the action of the hydrochloric acid. After the lapse of a longer or shorter time, the compound is produced; to isolate it, it is only necessary to saturate the mixture with carbonate of soda. It is purified by repeated washings and the usual processes.

The above-mentioned compounds are oleaginous, and scarcely, if

* Berzelius subsequently prepared the tartroglycerates.

† Mémoire sur l'acide butyrique, par MM. Pelouze et Gélis.—*Ann. de Chim. et de Phys.*, 3rd series, x.

at all, soluble in water. They are neutral substances, incapable of uniting immediately with the alkaline carbonates. Alkalies attack them slowly, saponifying them; in this way they all regenerate the acid from which they are derived, the glycerine being isolated. They may also be decomposed in an analogous manner by saturating their alcoholic solutions with muriatic acid, a process employed by Rochleder for the extrication of the glycerine from castor oil. In this manner, after a repose of twenty-four hours, glycerine and the æther of the acid employed are obtained. All that is necessary to separate the glycerine is the precipitation of the æther produced by water (except in the case of acetic æther) and the evaporation of the aqueous fluid. It still contains a little free acid, to get rid of which it is agitated with a little oxide of silver, and filtered after the addition of water. The concentrated fluid furnishes pure glycerine, presenting all its characters. I have reproduced it in this manner with each of the combinations formed with benzoic, valerianic, acetic and sebacic acids.

The acetic compound (*acetine*) is very distinctly soluble in water; it possesses an agreeable odour, similar to that of acetic æther, but much more permanent. Submitted to a carefully-conducted fractional distillation, it may be volatilized without sensible decomposition. After this operation, it preserves its pleasant odour, and presents the appearance of a limpid and colourless oil, possessing a taste which at first is saccharine like that of glycerine, afterwards acrid and ætherial. Treated with muriatic acid gas and alcohol, it is reduced, as before distillation, into acetic æther and glycerine. The mixture of acetic acid and glycerine, saturated at 212° F. with muriatic acid gas, only begins to furnish this substance after a week's repose. Several natural oils, examined by M. Chevreul and others, and especially cod-liver oil, yield acetic acid on saponification; it is possible that acetine may form one of the principles of these oils.

The valerianic compound (*valerine*) is more readily obtained; it possesses a peculiar, but faint, semi-ætherial, semi-valerianic odour. These are properties possessed by the *phocenine* of M. Chevreul, one of the principles of the oils of the dolphin, which is separable into phocenic or valeric acid and glycerine. The quantity of phocenine in these oils may amount to a fourth or a third of their weight.

The benzoic compound (*benzoïcine*) is formed in a few hours. It is more viscous than the two preceding. Its taste is aromatic and somewhat like pepper.

The sebacic compound (*sebine*) is formed in large quantity in twenty-four hours. It is an example of a neutral compound of a bibasic acid and glycerine.

The existence of these substances adds support to the facts already known, in showing that neutral fatty bodies really consist of fatty acids and glycerine.

The preceding compounds are not the only ones furnished by glycerine. I have already obtained several others, and hope to suc-

ceed in reproducing margarine and stearine, the most important of the glycerine compounds, and the principal constituents of the natural fatty substances.—*Comptes Rendus*, Jan. 3, 1853, p. 27.

Note on Quinidine. *By* L. Pasteur.

Several important memoirs have been published upon this alkaloid, which is associated with quinine and cinchonine in various cinchonas, and the sulphate of which is asserted to have been employed for some time in the adulteration of sulphate of quinine.

The results of these researches however present very striking contradictions. I believe I have removed all the difficulties by extracting two distinct alkaloids from some commercial quinidines; these differ greatly in their crystalline forms, degrees of solubility and rotatory power. One of them is anhydrous, the other hydrated. The mixture of these two alkaloids in different proportions has been the cause of all the contradictions attending the study of quinidine.

I confine myself now to presenting the details of two comparative experiments, determining the values of their absolute rotatory powers at a temperature of 55°·4 F. :—

Proportion of active matter	ϵ	0·0127026	0·0127026
Proportion of absolute alcohol at 55°·4 F.	e	0·9872974	0·9372974
Density of the fluid at 55°·4 F.	δ	0·78393	0·78393
Length of the tube	l	500^{mm}	500^{mm}
Deviation of the tint	α	12°·48↗	7°·2↖
Rotatory power for 100 mill.....	$[\alpha]j$	250°·75↗	144°·61↖

I may observe, that the alkaloid which causes a deviation to the right, *in a different direction to quinine*, and to a much more considerable degree, is the one which offers the most distinct analogy with quinine. All confusion of these two substances is therefore impossible.

I believe that M. Leers, in the investigation which he has recently published upon quinidine, had before him one of the pure alkaloids without admixture of the other. M. Van Heÿningen, on the other hand, has operated upon a mixture composed principally of the second alkaloid, which deviates the plane of polarization to the right. —*Comptes Rendus*, Jan. 3, 1853, p. 26.

On a Combination of Pelargonic Acid with Deutoxide of Nitrogen. *By* L. Chiozza.

The experiments of M. Cahours have shown that the carbonated hydrogen of the bitter oil of fennel combines directly with deutoxide of nitrogen, forming with this gas a crystallizable compound. This was hitherto the only instance of an organic substance containing deutoxide of nitrogen.

Wishing to obtain some pelargonic acid, by the oxidation of the essential oil of rue (*Ruta graveolens*, L.) according to the process

described by M. Gerhardt, I was led, in the course of this preparation, to the discovery of a combination of that acid with deutoxide of nitrogen, possessing very distinct acid properties, and forming with bases perfectly crystallizable salts.

The action of nitric acid upon the essential oil of rue has been studied by MM. Gerhardt and Cahours; and if the substance which I am about to describe did not present itself in the experiments of these distinguished chemists, the fact must probably be attributed to the nature of the essential oil employed by them; it is well known, in fact, that the presence or absence of certain carbonated hydrogens often modifies the action of nitric acid upon organic substances in a very remarkable manner.

The following is the method in which I operated. The oil was treated with its weight of commercial nitric acid diluted with its volume of water; in another case I employed pure nitric acid, but the results were the same. After three or four hours of ebullition, the oily stratum which floated on the surface of the acid was decanted, washed, and lastly treated with a concentrated solution of caustic potash. There was formed immediately a sort of syrup-like emulsion, strongly coloured, and holding in suspension a crystalline precipitate, which was increased by the addition of more water. The liquid was filtered, and the clear portion set aside for the preparation of pelargonic acid, which constitutes the principal part of the product; the precipitate was treated first with æther, to free it from a neutral oil which adhered to it, and then submitted to repeated crystallization from alcohol.

In a pure state it presents the form of magnificent square tables, of a fine yellow colour and very brilliant; it is very sparingly soluble in water and alcohol when cold, but dissolves readily in both those liquids when boiling. When heated suddenly, it fuses like a mixture of nitre and charcoal, leaving a residue of carbonate of potash.

Experiments showed me that this yellow precipitate is the potash salt of a new acid, to which my analyses gave the formula $C^9 H^{18} O^2$, $N^2 O^2$.

To isolate it, it is only necessary to dissolve the potash salt in boiling water, and to decompose the solution by means of a dilute mineral acid; the acid $C^9 H^{18} O^2$, $N^2 O^2$ then falls to the bottom of the vessel in the form of a very heavy oil, of a light yellow colour, and possessing a faint odour, which has no analogy with that of pelargonic acid. It only requires to be washed with boiling water and dried on the water-bath to obtain it quite pure. It cannot be dried over chloride of calcium, as it dissolves a small quantity of that substance.

On linen it produces a yellow spot; on paper a greasy spot, which disappears by heat. When a small quantity is heated in a test-tube to a certain point, an abundant disengagement of deutoxide of nitrogen mixed with combustible gases results almost instantaneously. This property of the acid renders its analysis rather difficult, and necessitates the employment of very long tubes.

The following are the results which I obtained :—

	Found.	Calculated.
Carbon	49·5	48·5
Hydrogen	8·4	8·2
Nitrogen.....	13·3	12·8

Other analyses gave numbers very close to these.

I should have liked to have been able to check the correctness of the formula which I attribute to this substance, by producing it directly by the action of deutoxide of nitrogen upon pelargonic acid; but the experiments which I undertook with this view did not lead me to any satisfactory result.

It may be, moreover, that the acid $C^9 H^{18} O^2$, $N^2 O^2$ is only formed by the action of potash on the products of the oxidation of the oil of rue; for I have always observed that the treatment with potash was accompanied by an elevation of temperature much more considerable than could be occasioned by the neutralization of the pelargonic acid. This can only be decided by future researches.

The most striking character of the acid $C^9 H^{18} O^2$, $N^2 O^2$ is the very slight solubility of all its salts in cold water.

The soda salt forms fine yellow laminæ, like the potash salt; a boiling saturated solution of this salt deposits nearly the whole of it on cooling.

The ammoniacal salt is scarcely more soluble than the preceding; it crystallizes in very brilliant elongated lamellæ. A paper soaked in the acid acquires a yellow colour, and loses its transparency when dipped into a solution of ammonia diluted with more than 1000 times its volume of water.

The baryta salt was obtained by double decomposition; it forms a very light yellow powder. 0·26 gr. of this salt gave 0·130 of sulphate of baryta, which represents 23·3 per cent. of barium. The formula $C^9 H^{17} BaO^2$, $N^2 O^2$ requires 23·9.

The silver salt exactly resembles the baryta salt in its appearance. When heated in the air, it takes fire and burns with a greenish flame, leaving a residuum of pure silver. 0·119 gr. of this salt left 0·040 gr. of silver, which gives 33·6 per cent. The formula $C^9 H^{17} AgO^2$, $N^2 O^2$ requires 33·2.—*Comptes Rendus*, Nov. 29, 1852, p. 797.

Note on the Kakodyle of Valerianic Acid. By Dr. W. Gibbs.

As the compounds of metals with organic radicals are becoming every day of more importance to the theoretic chemist, I am induced to mention in this place the results of some experiments made in November 1849 on the formation of new organic compounds containing arsenic. When valerianate of potash is distilled with an equal weight of arsenious acid, a heavy oily liquid passes over into the receiver, slightly yellowish in colour, and possessing a penetrating and highly offensive odour of garlic. With a solution of chloride of mercury this liquid gives a thick white precipitate, while the odour of garlic disappears, and is replaced by an agreeable aroma like that of valerianate of oxide of amyle. The oily liquid gave off thick white vapours in the air, but did not inflame.

Exposed for some time to the air in an imperfectly closed glass vessel, it became completely converted into a mass of large, brilliant, hard, four-sided prisms, which were nearly colourless, and after pressing with bibulous paper, free from smell. They had an acid reaction, and may have been the valerianic compound corresponding to kakodylic acid. These crystals were readily soluble in water. In an attempt to unite them with oxide of silver for the purpose of determining their constitution, they were completely decomposed. The oily liquid obtained by the distillation above mentioned was soluble in water, and appeared to reduce oxide of mercury to the metallic state. It will be seen that the reactions of the substance in question in all respects resemble those of the butyric kakodyle obtained by Wöhler, and exhibit much analogy to those of the acetic kakodyle of Bunsen. The offensiveness of these compounds to non-chemical noses belonging to persons occupied in the same building with the writer, has hitherto prevented a further investigation of this subject, which it is to be hoped will engage the attention of chemists more advantageously situated.—Silliman's *Journal*, January 1853.

Researches on Stannæthyle. *By* Prof. C. Löwig.

[Continued from page 113.]

Stannæthyle and its Compounds.—As appeared from the examination of the radicals, it is almost impossible, on account of their great agreement in physical and chemical properties, to obtain them, with the exception of stannæthyle, perfectly pure, even when sufficient material is at hand. The pure radicals cannot therefore be employed in the preparation of the compounds of stannæthyle. The following are the methods by which these compounds may be readily obtained without the necessity of previously separating the radicals.

First Method.—When the reaction which takes place between the iodide of æthyle and the alloy of tin and sodium is complete, and the ætherial solution of the whole of the products so formed has been prepared as previously directed, iodine is added to the solution as long as it is taken up thereby, with loss of its colour. The solution thus obtained of the iodine compounds in general is mixed with alcohol, and the æther then completely driven off. The collected iodine compounds are then converted into oxides by adding to their alcoholic solution, until complete decomposition takes place, freshly-precipitated, hydrated oxide of silver which has been washed with alcohol. These oxides form two classes. Those of the first class are soluble in alcohol; to these belong the oxides of methstannæthyle and æthstannæthyle. Those of the second class are insoluble in alcohol, and are precipitated with the iodide of silver. The whole is now filtered, and the iodide of silver with the insoluble oxides completely washed with alcohol. The alcoholic solution, which has a strong alkaline reaction, is exactly saturated with sulphuric acid previously diluted with alcohol, and the solution left to spontaneous evaporation. The sulphates of the oxides of methstannæthyle and æthstannæthyle are separated in the manner already

described by repeated recrystallization, and are thus obtained perfectly pure. The pure salts are again dissolved in alcohol, the solutions exactly decomposed by baryta-water, and the solutions of the oxides filtered from the sulphate of baryta. These solutions are then employed for the preparation of the pure salts.

The iodide of silver which separates, and which is mixed with the excess of oxide of silver and with the insoluble bases, is stirred with alcohol in a beaker until it forms a thin paste; strong muriatic acid mixed with alcohol is then added until it slightly predominates; the alcoholic solution of the organic chlorine compounds is then best separated from the chloride and iodide of silver by pressure between fine linen. As the chlorine compounds differ in solubility in alcohol, they separate gradually during spontaneous evaporation in this order: $(Sn^2 Ae^2)Cl$, $(Sn^1 Ae^3)Cl$, and $(Sn^1 Ae^4)Cl$. The pure oxides are thrown down from the pure chlorine compounds by ammonia, but not by potash.

This process can also be varied in the following manner:—The alcoholic solution of the collected iodine compounds is mixed with strong ammonia, by which the whole of the oxides, except those of meth- and æthstannæthyle are thrown down. The white precipitate is collected upon a filter, washed with alcohol, then dissolved in muriatic or any other acid (which however must be mixed with alcohol), and the mixture of salts separated by crystallization. In the alcoholic solution filtered from the oxides, the iodides of meth- and æthstannæthyle are still present. The solution is mixed with water, and the whole shaken with æther, which takes up the iodine compounds, the separation of which can then be effected by oxide of silver.

Second Method.—The ætherial solution of the radicals and iodine compounds is mixed with alcohol until the radicals begin to separate; a solution of nitrate (or sulphate) of silver with which alcohol has been mixed is then added until decomposition is complete, care being taken however that the silver salt is not in excess. For this purpose, small portions are filtered towards the end of the precipitation, so as to ascertain whether nitrate of silver still produces a precipitate. Before separating the precipitate by filtration, the whole is left standing in a tolerably warm place until the æther is completely volatilized. This is necessary because the nitric compounds of the oxides of stannæthyle are partly insoluble, or soluble with difficulty in æther mixed with alcohol; a portion of these compounds accordingly separates during the precipitation, which, if the liquid be filtered immediately, can only be extracted by alcohol from the precipitate of iodide of silver with great difficulty. But if the æther is evaporated before the filtration, the precipitated portions of the salts of stannæthyle can be readily dissolved again. The alcoholic solution of the nitrates is slowly evaporated to dryness on the water-bath. The residue is treated with æther, which furnishes small white crystals. If the latter are dissolved in hydrated alcohol and the solution slowly evaporated, crystals of nitrate of æthstannæthyle are first obtained, and afterwards crystals of nitrate

of stannæthyle. After the evaporation of the ætherial solution, a crystalline mass and an oily fluid are obtained; the latter, on cooling, is perfectly transparent and becomes solid. The crystalline mass is a mixture of the nitrates of elayl- and acetstannæthyle, and contains also a small quantity of nitrate of stannæthyle. The varnish-like residue consists of the nitrates of meth- and æthstannæthyle. If they are dissolved in anhydrous alcohol, and the solution digested with carbonate of baryta, the bases remain dissolved in the alcohol, and may be obtained in a crystalline form by evaporation.

Third Method.—The ætherial solution of the radicals and iodine compounds is mixed with alcohol, and exposed to spontaneous evaporation in a shallow glass vessel. A slow oxidation of the radicals takes place, and those which are insoluble in alcohol separate in the form of a white powder, whilst the iodine compounds and the oxides of meth- and æthstannæthyle remain dissolved in the alcohol. The separated oxides are dissolved in a mixture of alcohol and muriatic acid, and the chlorine compounds separated by crystallization. The separation of the iodine compounds from the oxides of meth- and æthstannæthyle is effected of course as already described.

The following observations on some compounds of stannæthyle may serve, as already observed, for its closer characterization. Their complete examination is the object of a separate investigation, the results of which will be made public at some future time.

Stannæthyle, SnAe.—The general properties of this radical have already been stated. It forms a thick oily fluid, which when pure appears colourless. At +10° F. it still retains its fluidity. Its spec. grav. is 1·558 at 59° F. It consists of—

Tin	1	=	59	67·08
Carbon	4		24	27·27
Hydrogen	5		5	5·67

Oxide of Stannæthyle, (SnAe)O.—If the ætherial solution of stannæthyle is allowed to evaporate in the air, its oxide separates in the form of a white, tasteless and inodorous powder. The oxide is precipitated from its combinations by ammonia. It is not volatile; if heated in contact with the air, it ignites, and burns with a bright flame, diffusing a thick cloud of oxide of tin. Analysis gave—

Tin	..	1	=	95	61·46
Carbon	25·09	4		24	25·00
Hydrogen	5·47	5		5	5·21
Oxygen	..	1		8	8·33

All the salts of the oxide of stannæthyle crystallize; they are difficult of solution in æther, but dissolve in alcohol and water. Potash precipitates the oxide, and when employed in excess, redissolves it. The salts are all inodorous.

Nitrate of the Oxide of Stannæthyle, (SnAe)O, NO^5.—This salt is obtained either by dissolving the oxide in dilute nitric acid, or by decomposition of the iodide of stannæthyle by nitrate of silver. It crystallizes in rather large crystals, fuses when heated, and burns with a slight explosion. For the determination of the nitric acid,

the solution of the salt was digested with carbonate of baryta, and the baryta precipitated from the filtrate by sulphuric acid. Analysis gave—

Tin	..	1	= 59	39·34
Carbon	15·66	4	23	16·00
Hydrogen	3·13	5	5	3·33
Oxygen	..	1	8	5·33
Nitric acid	34·93	1	54	36·00

Sulphate of the Oxide of Stannæthyle, (SnAe)O, SO^3.—This is obtained by the decomposition of iodide of stannæthyle with sulphate of silver. It is crystallizable, and soluble in water and alcohol. The salt, dried at 212° F., gave the following results on analysis:—

Tin	..	1	= 59	43·40
Carbon	17·20	4	24	17·64
Hydrogen	3·90	5	5	3·67
Oxygen	..	1	8	5·88
Sulphuric acid	28·78	1	40	29·41

Iodide of Stannæthyle, (SnAe)I.—Iodine is added to the ætherial solution of stannæthyle as long as its colour disappears on solution; the solution is then allowed to evaporate spontaneously. The iodide crystallizes in remarkably beautiful colourless needles, which are often 4 inches long. It is difficult of solution in water, but dissolves readily in alcohol and æther; it fuses on the water-bath to a colourless fluid oil. Slowly heated, it sublimes in very beautiful, light, acicular crystals, like benzoic acid. Some analyses of this salt have already been given. Subsequent analyses gave—

Tin	..	..	1	= 59	27·57
Carbon	10·90	11·46	4	24	11·21
Hydrogen	3·38	2·30	5	5	2·32
Iodine	58·89	58·89	1	127	58·80

Bromide of Stannæthyle, (SnAe)Br.—This is prepared directly, like the iodide. It crystallizes in remarkably beautiful needles, fuses readily, and behaves, with water, alcohol and æther, like the preceding substance. Analysis:—

Tin	..	..	1	= 59	35·12
Carbon	14·00	14·16	4	24	14·28
Hydrogen	3·23	3·02	5	5	3·00
Bromine	47·36	47·36	1	80	47·60

Chloride of Stannæthyle, (SnAe)Cl.—If a solution of oxide of stannæthyle in muriatic acid diluted with alcohol be allowed to evaporate in a shallow vessel, acicular crystals of a silvery whiteness, and of the length of the bottom of the vessel, are obtained. It fuses at as low a temperature as 86° F., and solidifies when quickly cooled into an amorphous mass; it is very volatile, and sublimes at a very low temperature even before fusion, depositing beautiful, hard, acicular crystals. In its properties it resembles the bromide and iodide. Analysis yielded—

Tin	..	..	1	=	59·0	48·35
Carbon.....	18·60	18·80	4		24·0	19·43
Hydrogen.....	4·80	4·00	5		5·0	4·06
Chlorine	28·30	28·25	1		35·5	28·86

Metylenstannæthyle, $Sn^2 Ae^2$.—The iodine compound of this radical separates first of all when the alcoholic solution of the mixed iodides is left to spontaneous evaporation. The chloride of the radical was also obtained twice in the same manner. The radical itself could not be isolated. The per-centage composition of the radical is the same as that of stannæthyle. Its atomic weight is 176.

Oxide of Metylenstannæthyle, $(Sn^2 Ae^2)O$.—This is precipitated from its combinations by means of ammonia, and exactly resembles oxide of stannæthyle.

Iodide of Metylenstannæthyle, $(Sn^2 Ae^2)I$.—This salt is difficult of solution in alcohol; its properties and composition have already been described.

Chloride of Metylenstannæthyle, $(Sn^2 Ae^2)Cl$.—This compound is difficult of solution in alcohol, and separates from its hot alcoholic solution in shining white laminæ. Its analysis gave the following results:—

Tin	..	..	..	2	118·0	55·79
Carbon.....	22·14	22·25	22·20	8	48·0	22·69
Hydrogen	4·86	5·00	5·02	10	10·0	4·74
Chlorine	17·06	16·84	16·84	1	35·5	16·78

Elaylstannæthyle, $Sn^4 Ae^4$.—As appeared from the investigation of the radicals, there still exist radicals in the cold alcoholic solution from which stannæthyle and acetstannæthyle have separated; these are thrown down by the addition of water, and become richer in carbon in proportion to the lateness of their precipitation. Thus five portions were gradually precipitated, of which the first contained 27·45, the second 28·08, the third 30·90, and the fourth and fifth between 34·72 and 34·42 per cent. of carbon. The last portions, after the radicals had been converted into iodine compounds and the alcoholic solution had been evaporated, left behind oily fluids, from which after long standing crystals of iodide of elaylstannæthyle separated. The radical of this compound forms the essential part of the third portion. It is perfectly colourless, oily, with a spec. grav. of 1·410. Its per-centage composition is the same as that of stannæthyle, and its atomic weight 352.

Oxide of Elaylstannæthyle, $(Sn^4 Ae^4)O$.—This oxide appears, like that of stannæthyle, as a snowy-white amorphous powder; it is thrown down from its combinations by ammonia in the form of a flocculent precipitate. It is also precipitated by potash, but dissolves again in a slight excess of that reagent. It is completely insoluble in water, but dissolves in small quantity in boiling alcohol, and still more readily in æther, separating again from the solutions however in the form of an amorphous powder. With acids it forms colourless salts, which are soluble in alcohol and æther, but which are precipitated from their alcoholic solution by a great addition of water; this serves to distinguish them essentially from the salts of

stannæthyle. In the dry state the salts are fatty, camphor-like to the touch, and possess a slight and peculiar odour. The oxide consists of—

Tin	4	=	236	65·55
Carbon	16		196	26·66
Hydrogen	20		20	5·55
Oxygen	1		8	2·24

Nitrate of the Oxide of Elaylstannæthyle, $(Sn^4 Ae^4)O, NO^5$.—This compound is obtained by dissolving the mixture of radicals which is thrown down from the cold alcoholic solution by water, and especially the portions last precipitated, in a mixture of alcohol and æther, decomposing the radicals exactly by means of nitrate of silver, and evaporating the fluid filtered from the silver precipitate by a gentle heat. After some time crystals are formed in the oily residue. These are pressed and then treated with æther, which leaves a portion undissolved. The nitrate of elaylstannæthyle crystallizes from the ætherial solution; only the last portions which separate, however, are the pure compound. The analysis of this salt gave the following results. The determination of the nitric acid was effected by digesting the alcoholic solution with carbonate of baryta:—

Tin	..	4	= 236	57·01
Carbon	22·23	16	96	23·14
Hydrogen	5·02	20	20	4·83
Oxygen	..	1	8	1·98
Nitric acid	13·43	1	54	13·04

Iodide of Elaylstannæthyle, $(Sn^4 Ae^4)I$.—This compound generally crystallizes in rhombic tables, but sometimes it is obtained in scaly and acicular crystals, which are fatty to the touch, and may be readily reduced to powder. It is completely insoluble in water, but dissolves readily in alcohol, and especially in æther. The mode of preparation of the salt and its composition have already been described.

Bromide of Elaylstannæthyle, $(Sn^4 Ae^4)Br$.—This compound, which agrees in its properties with the preceding, is obtained by saturating with bromine the mixture of radicals (see the nitrate) in solution in alcohol and æther, and then leaving the solution to evaporate spontaneously. Crystals are formed in the oily residue, which are pressed, and then recrystallized from their ætherial solution. The crystals which are last deposited are the compound, which however is only obtained quite pure by repeated crystallizations. Analysis gave—

Tin	..	..	..	4	=236	52·57
Carbon	21·40	22·22	22·17	16	96	22·27
Hydrogen	4·56	4·78	..	20	20	4·63
Bromine	18·08	18·08	18·28	1	80	18·53

Chloride of Elaylstannæthyle, $(Sn^4 Ae^4)Cl$.—This compound is the last to separate in crystals when the mixture of the oxides of the radicals is dissolved in muriatic acid and alcohol, and the solution left to spontaneous evaporation. In its properties it agrees with the preceding compounds. Analysis gave—

Tin	4 =	236·0	61·18
Carbon	16	96·0	24·76
Hydrogen	20	20·0	5·16
Chlorine	1	35·5	8·90

[To be continued.]

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the desilverizing of Argentiferous Lead by means of Zinc. By Dr. KARSTEN.

As early as 1842, the author made some fusion experiments with lead and zinc, and found that when a mixture of these metals was very slowly cooled, lead with a very small quantity of zinc collected at the bottom of the crucible, and zinc with a small per-centage of lead at the top. When the lead contained silver, he found that it was almost entirely transferred to the zinc; and upon subsequently learning that in Caermarthenshire, silver is separated from lead by means of zinc, he has resumed his experiments on the subject.

After having, in the first instance, ascertained that the silver may be perfectly separated from argentiferous lead by means of zinc, and at the same time observed several difficulties attending the process, he is of opinion that the following mode of operation gives the best results:—

A cast-iron tube, 1½ inch in diameter, is so adapted to the crucible that the desilverized lead may be drawn off from the bottom. One end of this tube, dipping nearly to the bottom of the crucible, is furnished with a slide moving in grooves at the edge of the crucible, so that it can be closed at pleasure by means of a rod. In this way the flow of melted lead may be regulated, and the fall of level in the crucible rendered gradual and uniform.

Into this crucible, 25 cwt. of lead containing $\frac{7}{8}$ of an ounce of silver to the hundredweight and 4 cwt. of zinc were introduced, and melted, and then stirred together during one hour while at a bright red heat. This high proportion of zinc to argentiferous lead was because it was intended to attempt a process of concentration, in which the same quantity of zinc should serve to desilverize subsequent charges of lead. After the stirring apparatus was taken out, and the fused metals kept for four hours at a red heat, the lead, perfectly desilverized, was drawn off until the contents of the crucible did not amount to more than 6 cwt. To this residue a second 25 cwt. of lead were added, and the operation repeated. With the third charge of lead, 2 cwt. of zinc were likewise added, for reasons which will be mentioned further on. A fourth, fifth, and sixth charge of lead were introduced, and similarly treated; to the fourth charge, 2 cwt. of zinc were again added. The lead drawn off in each instance was perfectly desilverized. When however a seventh charge was introduced without an addition of zinc, the lead, when drawn off, still retained silver to the amount of $\frac{3}{8}$ of an ounce in

the hundredweight. The desilverizing of 150 cwt. of this lead required therefore 8 cwt. or $5\frac{1}{3}$ per cent. of zinc, a quantity which differs widely from that indicated by previous experiments, viz. $1\frac{1}{2}$ p. c.

An addition of $1\frac{1}{2}$ per cent. of zinc is quite sufficient for the perfect desilverization of lead when only one charge is worked. Thus, for instance, 25 cwt. of lead may very well be desilverized by 42 lbs. of zinc; but the difficulty of separating the small quantity of argentiferous metal from the desilverized lead is so great, that this plan is not practicable. Again, on the other hand, there is a certain limit to the magnitude of the melting vessel which cannot be exceeded, and consequently recourse must be had to a concentration process. The separation of the silver from the lead is very imperfect, if twice or three times as much zinc as is requisite for one charge of lead is added at once, with a view of making it serve for several charges. It is likewise imperfect, when, on introducing into the crucible the several charges of lead, the $1\frac{1}{2}$ per cent. of zinc requisite for desilverizing it is added with each charge. If, therefore, with reference to the above example, the first melting is made with 25 cwt. of lead and 42 lbs. of zinc, the second, third, fourth, &c. charges (added to the residue in the crucible) must also consist of 25 cwt. of lead and 42 lbs. of zinc.

The cause of the unfavourable result of the mode of desilverizing attempted by the author lies in the necessity for stirring the melted metals. The oxidation of the lead and zinc at the surface of the mass is very disadvantageous.

In order to ascertain whether the lead employed in this process was in any way deteriorated by the small quantity of zinc which it takes up, the author examined the different layers into which the metals separate. The crucible, which, after the metals have been stirred, is allowed to rest until the lead is ready to be drawn off, contains a series of layers of metallic mixtures in which the proportions of lead and zinc vary greatly. In the experiments in question, the following relations were observed:—The uppermost layer containing the largest proportion of silver, contained likewise, besides zinc, 2 per cent. of lead. The per-centage of zinc, and at the same time that of silver, decreased in the successively underlying layers in the same proportion as the per-centage of lead increased. A specimen taken at about $1\frac{1}{4}$ inch below the surface contained 8·6 per cent. of zinc; $\frac{1}{2}$ an inch deeper the per-centage of zinc was 2·5, and a little below this was the desilverized lead, containing $\frac{3}{4}$ per cent. of zinc throughout. It appears therefore that the lead, when in contact with zinc, takes up and retains $\frac{3}{4}$ per cent. of zinc, even under circumstances most favourable for their separation. The per-centage of zinc in the desilverized lead is always from $\frac{3}{4}$ to 1 per cent., and does not appear to be influenced by the greater or less quantity of lead with which it is fused in the first instance. Experiments in the distillation muffle proved that the lead obstinately retains a portion of zinc even at a high temperature. Small as the quantity of zinc is which remains in the lead, it might perhaps be prejudicial in many instances to the introduction of this process for

separating the silver. It cannot be denied that even $\frac{3}{4}$ of a per cent. of zinc communicates to the lead some degree of brittleness, which renders it less applicable than pure lead to many purposes, such as the construction of tubes. For the preparation of white lead, it does not appear to have any disadvantage; but, on the other hand, it is asserted that lead containing this quantity of zinc cannot be employed in the fabrication of shot. In the case of some lead works, where pure lead cannot be obtained, a greater impregnation of the lead with zinc, to the extent of $\frac{1}{4}$ of a per cent., would not perhaps be of any importance; and the application of zinc to desilverize the lead produced there would be very desirable, if any means can be found of obviating the necessity for stirring, as well as the formation of oxide.

The argentiferous zinc obtained by this process always retains a portion of lead, which is sufficient for the refining of the silver after the zinc has been separated from the mixture, and the alloy of silver and lead remains in the distillation muffle. If the per-centage of lead is not sufficient for this purpose, more must be added, in order that in the distillation vessels the silver may be accumulated in the lead, which is afterwards to be cupelled.

The distillation does not present any difficulties when suitable muffles are employed. The results obtained with such muffles as are employed in Upper Silesia were, on the contrary, very unsatisfactory. The author had muffles constructed, which, with the exception of a slit $\frac{3}{4}$ths of an inch in diameter, were quite closed for a height of 4 inches from the bottom. The slit could be closed and reopened in the usual manner, when, after the distillation was completed, it was necessary to draw off the remaining argentiferous lead. Such a muffle was charged for each distillation with 1 cwt. of the metallic alloy, consisting of zinc, lead and silver. The product of four distillations of a mixture, which, according to the most careful assays, contained $47\frac{1}{4}$ oz. of silver, was 242 lbs. of lead and $44\frac{8}{44}$ oz. of silver. The loss of silver amounted therefore to $3\frac{1}{22}$ oz.; but this is chiefly owing to the scattering of small globules in the muffle, and partly remains in the scum, from which it may be again recovered by the subsequent distillations, by washing, and other appropriate means.

The author is of opinion that the small loss experienced in the desilverizing of lead by means of zinc is an essential advantage as regards its application to poor argentiferous lead, which will not pay the cost of cupellation, for the silver may be profitably extracted by the zinc process, if the unavoidable retention by the lead of a small per-centage of zinc admits of its being adopted at all. This per-centage of zinc may be separated from the lead by remelting in the refining furnace.—*Polytechn. Centralblatt*, 1853.

On the Determination of the Commercial Value of Indigo.
By M. Wittstein.

Wittstein advocates the use of the deoxidation test proposed by Berzelius and Pugh, and considers that the discredit into which it

has fallen is the result of unfounded prejudice. He further points out the several defects of the other modes of testing indigo. The use of sulphuric acid as a solvent of the blue colouring matter is objectionable,—first, because it takes up other constituents of indigo, partly organic, and worthless as dyeing materials, partly inorganic; secondly, because there is no means of separating the indigo-blue from the other dissolved substances. He considers the method proposed by Reinsch*, of determining the commercial value of indigo by observing the intensity of colour of the sulphuric acid solution at a certain definite point of dilution as of small value, inasmuch as it gives only relative results, and that with no very great accuracy. Of the actual per-centage of blue colouring matter it gives no indication.

The use of chlorine he considers as still more open to objection,—in the first place, because it furnishes only relative results, and in order to obtain absolute results, it must be ascertained how much chlorine a certain weight of pure indigo-blue requires for its decolorization; secondly, commercial indigo contains various other organic substances, coloured and colourless, which likewise take up chlorine; consequently the per-centage of indigo-blue, calculated from the quantity of chlorine consumed, is always too high and requires correction, for it cannot safely be assumed that the chlorine acts first upon the indigo-blue.

In order to obtain some positive data connected with the use of the chlorine test, Wittstein made some experiments to determine the quantity of chlorine requisite for the decolorization of a certain weight of pure indigo-blue, assuming at the outset that this quantity was constant. He was, however, unable to arrive at any practically available results. He used the solution of indigo highly diluted; the operation was conducted in a long-necked flask, in order to avoid any interruption of the action by the renewal of water which had evaporated, and the solution of salt was added at regular intervals; notwithstanding all these precautions, the quantities of chlorate of potash requisite to produce decolorization in several successive experiments were very unequal. He considers that these discrepancies are dependent upon circumstances with which we are not sufficiently acquainted; for instance, the duration of the process, a small quantity of salt producing as great an effect in a certain time as a larger quantity in a less time; but when the reaction occupies too long a time, the liquid becomes concentrated and the result impaired. The decolorization of weak solutions cannot be effected at the ordinary temperature, and concentrated solutions are decolorized at the ordinary temperature only after the lapse of some time; if they are employed at an elevated temperature, the discrepancy in the results is increased still more.

Wittstein therefore comes to the conclusion, that the old reduction-test should be again adopted, since it furnishes not merely relative, but absolute and tangible results, which, when a few precautions are taken, are very trustworthy. It is moreover easy to carry

* Jahrb. für Prakt. Pharm., xviii. p. 248.

out, and does not occupy more than two days. He gives the following directions for its application:—

10 grs. of indigo are rubbed with water in a porcelain mortar, to this 20 grs. of hydrate of potash are added, together with a few drops of water, the rubbing being continued, and then 40 grs. of sulphate of iron, the mass mixed with water, so as to form a thick paste, and introduced into a six-ounce stoppered bottle, which has been previously weighed; the mortar should then be rinsed, and the bottle nearly filled up with water. After inserting the stopper, the whole is weighed and well shaken for some time. After the lapse of a few hours, the indigo is decolorized and dissolved. The mixture is then allowed to settle, the clear liquid is poured into a glass cylinder as completely as possible, and the bottle again weighed. The clear liquid is then to be treated with hydrochloric acid, the blue precipitate collected upon a weighed filter, washed with water, dried and weighed. By means of a proportion it may be ascertained how much indigo-blue is contained in the 10 grs. of indigo; if, for instance, the contents of the bottle weighed 3140 grs., the residue left on decantation 535 grs., and the 2605 grs. of clear liquor yielded 2·5 grs. of indigo-blue, then—

$$2605 : 3140 = 2{\cdot}5 : x$$

$$x = 3{\cdot}01.$$

Consequently the indigo examined would contain 30·1 per cent. of pure colouring matter.—*Vierteljahresschrift für Prakt. Pharmacie;* and *Pharmaceutical Journal*, March 1853.

PROCEEDINGS OF SOCIETIES.

Royal Institution.

January 28, 1853.

"On Gerhardt's discovery of Anhydrous Organic Acids," by Professor Williamson.

The discovery by M. Gerhardt of a number of anhydrous organic acids has thrown so much light on one of the most important questions of chemical philosophy, that it constitutes one of the most remarkable illustrations of the manner in which the rich materials of organic chemistry may be brought to bear on the explanation of the phænomena of chemical action and the laws of chemical combination.

It is not unworthy of remark, that the bodies prepared by Gerhardt had for some years past been supposed to exist ready formed in combination with water and other bases, and that the chief objection to that supposition was founded on the circumstance of their never having been separated from such combination, and presented in an isolated form. In fact, Gerhardt has supplied the very link in the chain, which was expected to constitute evidence for a familiar theory of the constitution of salts. But the process by which the result was attained is even more important than the result itself, and has led to our drawing from that result a conclusion different from that which was generally expected. Chemistry aims at dis-

covering the nature of that action by which substances of opposite properties undergo those remarkable changes which we call chemical combination; and it naturally follows from this view of its objects, that chemical science is more advanced by the discovery of a new *process* than by the discovery of a new *substance*; and its theories are more immediately affected by the nature of a process of change than by any physical fact, such as the existence of a peculiar body or class of bodies. Thus it is that the method of isolating the anhydrous organic acids has afforded evidence of a new view of the constitution of acids and salts.

A few words may serve to give an idea of the previous state of the question.

Compounds of oxygen acids were supposed to consist of the anhydrous acid united with an oxide. Thus hydrated sulphuric acid was represented as containing the anhydrous group SO^3 plus an atom of water, H^2O; and in the saturation of this hydrated acid by a base such as potash, it was conceived that this oxide replaced the water. The existence of anhydrous sulphuric acid in an isolated state, and the fact that it so readily combines with water, was urged as an argument in favour of this theory; and the same holds good with phosphoric, carbonic, sulphurous, lactic, nitrous, and even (according to the recent discovery of Dessaignes) nitric acid.

However simple this view might appear, and however satisfactory it might be in explaining those cases of combination for which it was specially intended, chemists soon became acquainted with bodies perfectly analogous in their general properties to the oxygen acids, and producing by their action upon bases similar effects, but which, from the fact of their containing no oxygen, could not possibly be conceived as made up of water and an anhydrous acid. For instance, hydrochloric acid was proved, both analytically and synthetically, to be composed of nothing but chlorine and hydrogen; and when it combines with potash, the hydrogen is found to leave the chlorine, whilst potassium takes its place.

Being desirous of simplifying as far as possible their views of these phænomena, and of extending the same explanation to all like cases, certain chemists were led to imagine a new mode of representing the constitution and reactions of oxygen acids, which had the advantage of connecting the two classes of analogous reactions by the same theory. This consisted in conceiving, that in the formation of a hydrated acid, a compound radical is produced in combination with hydrogen; so that hydrated sulphuric acid is the hydrogen compound of SO^4, in the same way as hydrochloric acid is the hydrogen compound of chlorine. There were many arguments in favour of this view, amongst which the most prominent was derived from the fact, that when a salt of the one class, as chloride of potassium, decomposes a salt of the other, as sulphate of silver, the result is exactly in conformity with what must occur on the supposition of the compound radical; and in like manner, the electrolytic decomposition of a sulphate moves the group SO^4 to the positive pole, where it either combines with a metal or undergoes decomposition.

One of the strongest arguments against the view that the oxygen acids contain water, is afforded by the results of recent researches (especially of MM. Laurent and Gerhardt) on the atomic weight of acids. Those chemists have rendered more definite and exact than they had been before our ideas on the distinctions between monobasic, bibasic and tribasic acids, and have clearly established that the correct expression of the atom of nitric acid must be such as contains half as much hydrogen as is contained in 1 atom of water (inasmuch as water is bibasic, and nitric acid monobasic). Of course this proportion may be as well established by doubling the atomic weight of water as by halving that of hydrated nitric acid; but either way it is clear that hydrated nitric acid cannot *contain* water.

Such was the position of the question, when an English chemist proved that the formation of æther from alcohol (which was considered chemically as the hydrate of æther) does not consist in a separation of two already-formed compounds, but in a substitution of hydrogen by the organic radical æthyle. A similar fact M. Gerhardt has proved respecting a great number of organic acids, by preparing bodies which stand to them in the same relation as æther does to alcohol.

The researches of M. Cahours had led to the discovery of a series of bodies necessary for Gerhardt's process. These were obtained by the action of pentachloride of phosphorus on various hydrated organic acids, and consisted of chlorine combined with the oxygenized radical of the acid. Thus from benzoic acid was prepared the chloride of benzoile, $C^7 H^5 OCl$, and the corresponding bodies from cuminic, cinnamic, and various other acids. Gerhardt has since made by the same process the body $C^2 H^3 OCl$, which is the chloride of the radical of acetic acid, called *othyle*. Now on bringing any one of these chlorides in contact with the potassium salt of the corresponding acid, the chemical force of combination between chlorine and potassium induced the decomposition.

These results can be most simply stated in the form adopted by M. Gerhardt, the discoverer, which consists in comparing the composition of these bodies with that of water, from which they are formed by the substitution of one or both atoms of hydrogen by organic radicals.

Thus water being represented by the formula $\begin{matrix} H \\ H \end{matrix} O$, acetic acid is formed from it by the action of chloride of othyle, $C^2 H^3 OCl$, which forms $\begin{matrix} C^2 H^3 O \\ H \end{matrix} O + HCl$, *i. e.* hydrated acetic acid and hydrochloric acid. If a second atom of chloride of othyle is made to act upon this acetic acid, or better upon the acetate of potash, $\begin{matrix} C^2 H^3 O \\ K \end{matrix} O$, we get, besides chloride of potassium, a compound, $\begin{matrix} C^2 H^3 O \\ C^2 H^3 O \end{matrix} O$, which, when compared to the original type, may be considered as water having both its atoms of hydrogen replaced by the radical othyle, $C^2 H^3 O$. This compound is the anhydrous acetic acid, which might

be called the acetate of othyle, inasmuch as that radical has, in the formation of the compound, taken the place of the basic potassium in the acetate of potash.

In like manner the anhydrous benzoic acid, $\begin{matrix} C^7 H^5 O \\ C^7 H^5 O \end{matrix} O$, was made by the action of the chloride of benzoile, $C^8 H^5 OCl$, on the benzoate of potash. It is a crystalline body, perfectly neutral to test-paper, scarcely soluble in water, readily soluble in alcohol and æther. On continued boiling with water, it is converted into hydrated benzoic acid, 1 atom of the anhydride with 1 atom of water forming 2 atoms of the hydrated acid by an interchange of hydrogen and benzoile. Besides several of these anhydrous acids, Gerhardt has prepared some intermediate acids, analogous to the intermediate æthers, by combining two different radicals in the same group. Thus chloride of benzoile with cuminate of potash, $\begin{matrix} C^{10} H^{11} O \\ K \end{matrix} O$, formed cuminate of benzoile, or benzocuminic acid, $\begin{matrix} C^{10} H^{11} O \\ C^7 H^5 O \end{matrix} O$; and in like manner several other intermediate acids were prepared.

In conclusion, the lecturer alluded to a feature of the development of the human mind in scientific research, which is strikingly illustrated by the substance and form of these results, and of which instances are probably to be found in the history of many others. The explanation of the above reactions consists in a combination of two modes of reasoning, which were developed by different schools, and for many years were used independently of one another. Gerhardt, to whose researches and writings some important steps in the doctrine of types are owing, formerly believed the truths which he saw from that point of view to be incompatible with the idea of radicals; but he now joins those chemists who find in each of these notions a necessary and most natural complement to the other.

May we not hope that such may be the result in other cases of difference of opinion on scientific questions, which the progress of knowledge will show to have been owing to the incompleteness and one-sidedness of each view, rather than to anything absolutely erroneous in either?

Chemical Society of London.

Feb. 7th, 1853. (Col. Philip Yorke, Vice-President, in the Chair.) The following paper was read:—

"On the mode of estimating the Value of Red Prussiate of Potash, and of testing the Strength of Bleaching Liquors," by Francis Lieshing.

1. For the estimation of red prussiate of potash, the author recommends the use of sulpharseniate of sodium, which is easily prepared either by dissolving pentasulphide of arsenic in liquid sulphide of sodium, or by dissolving arsenious acid in boiling caustic soda, and adding from time to time a concentrated solution of sulphur in caustic soda, until they cause no further precipitation of sulphur. Pale yellow crystals are formed on the cooling of the fil-

tered solution, and these are to be purified by recrystallization until they dissolve without residue. The composition of this salt is represented by the formula $3NaS, AsS^5+15HO$. It may be kept in solution for a considerable length of time without undergoing decomposition, especially when mixed with pure carbonate of soda or potash. It is decomposed by all acids, by chlorine, and by red prussiate of potash.

When a solution of red prussiate of potash is mixed with a solution of the sulpharseniate, a decomposition takes place, in which it is probable that 3 equivs. of ferridcyanide of potassium take 3 equivs. of sodium from an equivalent of sulpharseniate of sodium, setting free 3 equivs. of sulphur and 1 equiv. of pentasulphide of arsenic, and forming 6 equivs. of ferrocyanide of potassium, in which 3 equivs. of potassium are replaced by 3 equivs. of sodium. If however the sulpharseniate has been made alkaline by the previous addition of carbonate of soda, 3 further equivs. of sodium will be derived from this source, which will convert another 3 equivs. of ferridcyanide into ferrocyanide.

Assuming thus that 6 equivs. of red prussiate of potash would be converted into 12 equivs. of yellow prussiate of potash by the action of 1 equiv. of sulpharseniate of sodium and 3 equivs. of soda, calculation would show that for every 100 grs. of pure red prussiate of potash, 20 grs. of crystallized sulpharseniate of sodium are required, and this is the exact proportion which has been found by experiment to be required.

In conducting the process for the estimation of red prussiate of potash, 100 grs. of this salt are dissolved in 2 oz. of water, and a separate solution of 20 grs. of sulpharseniate of sodium, together with 40 or 60 grs. of pure carbonate of soda or potash, in 400 measures of water, is made, and introduced into an alkalimeter-tube. Each measure will thus contain one-twentieth of a grain of the sulpharseniate, and will indicate one-fourth per cent. of pure red prussiate. The mixture, as the decomposition takes place, acquires a pure white colour; and when this has been attained, the liquor is tested with a decoction of cochineal, which, on being added, is decolorized if the transformation of the red prussiate has not been completed; but when the transformation is complete, the cochineal colour is imparted to the solution.

2. For estimating the strength of bleaching powder and bleaching liquors, the author states that a solution of sulpharseniate of sodium might be used; but he prefers using a solution of arsenious acid in solution of carbonate of soda with excess of the latter. This solution is used with decoction of cochineal, as in the other case.

69·78 grs. of pure arsenious acid, corresponding to 50 grs. of chlorine, are dissolved with half an ounce of carbonate of potash in 200 measures of water, and put into an alkalimeter tube. Each measure will thus correspond with $\frac{1}{4}$ gr. of chlorine. On the other hand, 100 grs. of dry chloride of lime are mixed with 6 or 8 oz. of water, and to this the test-liquor is added until decoction of cochineal ceases to be decolorized.

THE CHEMICAL GAZETTE.

No. CCLII.—April 15, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Reactions upon which the American Amalgamation Process depends, and on the Extraction of Silver by means of Amalgamation. *By* Dr. KARSTEN.

THE remarks of Malaguti and Durocher upon several of the reactions connected with the process of amalgamation have induced the author to institute further experiments with the substances between which these reactions take place. He has observed the behaviour of the following bodies at a temperature ranging between 54° and 68° F.:—

Chloride of Copper and Metallic Silver.—When the chloride is dissolved in ammonia, no reaction takes place. When water or an aqueous solution of chloride of sodium is employed as the solvent of the chloride of copper, chloride of silver is formed, and the chloride of copper is converted into subchloride. This change is very slow when water alone is employed, and is remarkably accelerated by the addition of chloride of sodium.

Chloride of Copper and Metallic Copper.—Whether the chloride is dissolved in ammonia water or a solution of chloride of sodium, a quantity of copper is always dissolved sufficient to convert the chloride into subchloride.

Chloride of Copper and Metallic Zinc.—In all cases zinc precipitates metallic copper from the solution of chloride.

Chloride of Copper and Metallic Iron.—When the chloride is dissolved in ammonia, no action takes place even after the lapse of several weeks. From an aqueous solution of chloride of copper with or without chloride of sodium, copper is but very slowly and imperfectly precipitated.

Lead, bismuth, tin, and arsenic behave towards the ammoniacal solution of chloride of copper in the same manner as iron. When these metals are brought in contact with an aqueous solution of chloride of copper, it is converted into the subchloride, when there is not, as the author has formerly shown, any precipitation of metallic copper.

Chloride of Copper and Sulphuret of Silver.—When the chloride is dissolved in ammonia, no reaction takes place. When the solvent was water, no reaction could be detected even after the lapse of four months, during which time the mixture was frequently shaken. When, however, a saturated solution of chloride of sodium is em-

ployed as the solvent, after a few days a very gradually progressive and imperfect decomposition commences, chloride of silver and subchloride of copper being formed, with separation of sulphur from the sulphuret of silver, probably in a free state. The precise nature of the change in this slow process of decomposition is very obscure, because the subchloride of copper reacts as it is formed upon the sulphuret of silver, although much more slowly than the chloride. The sulphuret of silver was artificially prepared.

Chloride of Copper and Sulphuret of Copper.—The sulphuret was artificially prepared, and its composition was analogous to that of copper glance. When the chloride was dissolved in ammonia, no reaction was recognizable after the lapse of twenty weeks, during which time the mixture was frequently shaken. When, on the contrary, a solution of chloride of sodium is employed as the solvent, a reaction soon takes place, subchloride of copper being formed, which, when the vessel is so closed as to exclude atmospheric air, remains undecomposed. The perfect decomposition of the sulphuret of copper could not be effected, and would probably require an extremely long time. It is therefore difficult to decide whether sulphur is liberated, or whether a part of the sulphuret of copper is converted into a higher sulphuret.

Chloride of Copper and Sulphuret of Zinc (*Native Blende*).—The solutions of chloride in ammonia, water, or solution of chloride of sodium are gradually decomposed. It is probable that there is a complete interchange of constituents, giving rise to the formation of chloride of zinc, subchloride of copper and sulphuret of copper.

Chloride of Copper and Sulphuret of Lead (*Native Galena*).—The solution of chloride with chloride of sodium is but very slowly and imperfectly decomposed, with formation of subchloride of copper and chloride of lead.

Chloride of Copper and Compound Metallic Sulphurets, rich in Silver.—The solution of chloride with chloride of sodium is decomposed within a few days by stephanite, pyrargyrite and gray copper. The latter requires the longest time. Subchloride of copper and chloride of silver are formed.

Chloride of Copper and Chloride of Silver have no action upon each other, either in an ammoniacal or concentrated chloride of sodium solution.

Subchloride of Copper and Chloride of Silver.—When one or both substances are dissolved in ammonia, the subchloride is instantaneously converted into chloride, and the silver perfectly precipitated in the metallic state. When one substance is dissolved in ammonia, and the other in a concentrated solution of chloride of sodium, the result is precisely the same. When, on the contrary, both substances are brought together in solution with chloride of sodium, no reaction takes place any more than when water is employed as the solvent of the subchloride.

Subchloride of Copper and Sulphuret of Silver.—When ammonia is present, no action is recognizable after the lapse of six weeks. When, however, the subchloride of copper is dissolved in a solution

of chloride of sodium, even within a few days chloride of silver is found in the liquid and sulphuret of copper in the sediment.

Subchloride of Copper and Sulphuret of Zinc.—The subchloride is decomposed, chloride of zinc is formed, sulphur liberated, and metallic copper separated.

Subchloride of Copper and Sulphurets of Copper, Bismuth, or Antimony have no action upon each other.

Sulphuret of Copper and Chloride of Silver.—When the latter is dissolved in ammonia, decomposition soon commences, metallic silver, chloride of copper, and sulphuret of copper resulting. When the chloride of silver is dissolved in a solution of chloride of sodium, no reaction takes place.

Sulphuret of Zinc and Chloride of Silver.—In the presence of ammonia, chloride of zinc is very soon formed, and the silver appears to combine with sulphur. When a solution of chloride of silver with chloride of sodium is brought together with sulphuret of zinc, the reaction takes place more slowly.

Sulphurets of Lead or Bismuth do not show any reaction with chloride of silver, whether ammonia or solution of chloride of sodium is employed as the solvent.

It undoubtedly follows from these facts, that in the American process of amalgamation not a single reaction takes place by which metallic silver is formed, but that the formation of chloride of silver is the only result. Consequently the theory of the amalgamation will, notwithstanding the opposing statements of Malaguti and Durocher, remain the same as at its establishment twenty-three years ago, with the exception of a small and not very essential extension with regard to the reaction of subchloride of copper upon sulphuret of silver, as the subchloride is rapidly altered by the unavoidable access of air into an oxychloride, whose action upon sulphuret of silver is still problematical.

If however such is the state of things in the course of the process, it is obvious that very rich residues and a very considerable loss of mercury must be the necessary consequences of the process. The greater part of the silver obtained from the ores is undoubtedly united with the mercury by means of the direct action of the latter upon sulphuret of silver. Even any improvement upon the American process appears very doubtful, and could perhaps only consist in not incorporating the montons until after the action of the chloride of sodium and the magistral had taken place, thus delaying this operation as long as possible, and in using during the incorporation not only mercury, but likewise a quantity of iron filings or clippings. Least of all is there any ground for entertaining the opinion that the extraction of the silver from the ore can be effected by the saltierra and magistral, and that a saturated solution of chloride of sodium may be substituted for the mercury. When the ores from which silver is to be extracted by means of the American amalgamation process likewise contain argentiferous copper minerals, these latter will contribute only in a small degree to the total yield of silver, that is, proportionate to the decomposition of the ore by

chloride of copper. But a perfect decomposition would require a considerably larger addition of magistral than is necessary for the true silver ores, or than could be used without causing a very great loss of mercury.

By far the greater part of the silver annually produced is, in Europe at least, extracted not from silver ores, but from argentiferous ores of lead and copper. There is no more advantageous method of treating the richer silver ores than that in which lead is employed. According to the present state of metallurgical knowledge, poor silver ores may be most profitably worked by the process of solution with chloride of sodium. But it is this latter process alone that should be adopted for poor argentiferous copper ores, so as to obviate the treatment with lead, which, whether applied directly during the smelting of the ores, on the melting of the matts, or on the treatment of the raw copper, always gives the most disadvantageous results, and recalls to mind the infancy of metallurgy. The preliminary operations of the process of solution moreover possess the great advantage of accumulating in the most perfect manner the silver in the matts, the material upon which the operation of extraction is conducted. A still greater simplification of the process of solution will be effected, and still more profitable results will be obtained by discontinuing the conversion of the sulphuret of silver in the matts into chloride, and extracting by simple lixiviation the sulphate of silver formed from the sulphuret during the roasting. Hot water may then be substituted for the solution of chloride of sodium, and the silver precipitated from the solution by means of copper and iron.

Ziervogel, of the "Gottesbelohnungshütte" near Hettstadt, has made a very ingenious and correct application of the fact, that sulphate of silver requires a higher temperature for decomposition than any of the other metallic sulphates formed during the roasting; and he consequently continues the operation only so long as is necessary to effect the decomposition of these sulphates. The success of this process requires that the roasting should be conducted with extreme caution. Hitherto the perfect desilverization of the matts by this means has not been effected, the copper subsequently obtained containing as much as $\frac{3}{4}$ of an ounce in the hundredweight. This loss of silver is undoubtedly a consequence of excessive roasting. It is, moreover, difficult to suppose that it can be altogether avoided; and since the matt, as well as the residues of the amalgamation process, must be treated with chloride of copper and saturated solution of chloride of sodium in order to extract the remainder of the silver, it is improbable that such a process can be advantageously adopted. —*Polytechn. Centralblatt*, 1853.

On the Preparation of Crude Pelargonate of Oxide of Æthyle.
By Dr. Rudolph Wagner.

It was believed until very recently that œnanthylic æther is contained in the rind of the quince. New investigations, however, lead to the supposition that the odoriferous principle of the quince consists

of the æther of pelargonic acid. The method of forming pelargonic acid from oil of rue and nitric acid may be advantageously employed for the preparation of crude pelargonate of oxide of æthyle, which, like the fruit essences prepared by Döbereiner and others, will be found useful in perfumery, on account of its extremely pleasant odour.

For the preparation of this fluid, which may be called essence of quinces, oil of rue is treated with twice its quantity of very dilute nitric acid, and the mixture heated to the boiling-point. After a considerable time, two layers are observable in the fluid, namely an upper brownish layer, and a lower one, which consists of products of the oxidation of the oil of rue and the excess of the nitric acid. The lower stratum is freed from the greater part of the excess of nitric acid by evaporation on the chloride of zinc bath. The white flakes (probably sebacic acid), which occur plentifully in the acid fluid, are separated by filtration. The acid fluid is mixed with alcohol, and digested for a considerable time at a moderate heat, by which a fluid of a very pleasant quince-like odour is formed: this is purified by distillation. The preparation of the alcoholic solution of pelargonic æther might be still more advantageously effected from oleic acid (by Gottlieb's process).—*Chem. Pharm. Centralblatt*, Feb. 9, 1853, p. 94.

On a probably new Element with Iridosmine and Platinum, from California. *By* Dr. F. A. Genth*.

I received from Dr. Charles M. Wetherill a small quantity of white grains, which were collected in 1849–50 from California gold by the late Jos. R. Reynolds, Esq. An examination of these grains furnished me with results which are perhaps worth noticing.

I. When treated with boiling hydrochloric acid, two grains began to dissolve, with disengagement of hydrogen. As soon as I observed this reaction, I picked them out and washed them with water. With a good magnifying glass, I found that they were mechanically mixed with gold. Their colour was between a tin-white and steel colour. They were malleable, but harder than tin. They dissolved in nitric acid, yielding a crystalline salt, the native gold which was mixed with them remaining undissolved. They precipitated copper from solutions but slowly. Hydrosulphuric acid produced a brown precipitate in the solution in nitric acid. A pure piece of the metal before the blowpipe on charcoal fused readily. It was soon covered with a black oxide, and gave no incrustations. Borax in the oxidizing flame dissolved it, and gave a colourless bead, which on cooling became opalescent; the same reaction took place more readily in the reduction flame.

The quantity of this metal was too small for further experiments, but these reactions show that it is neither tin nor any other known element, although it has some relations to tin; but it is distinguished from it—

* From the Proceedings of the Acad. Nat. Sci., Philad., Dec. 1852, p. 209.

1. By its solubility in nitric acid.
2. By its brown precipitate with hydrosulphuric acid.
3. By not being readily oxidized before the blowpipe into a white oxide, and by its other blowpipe reactions.

May not the grains of native tin observed by Hermann in the auriferous sands from Siberia be the same substance?

II. An examination of the white grains, which were insoluble in hydrochloric acid, gave (after a few scales of native gold had been extracted by quite diluted aqua regia) the following results:—

Of 0·9366 grm., 0·4625 grm., or 49·4 per cent. were sisserskite ($IrOs^4$), in brilliant lead-coloured scales, some of which were imperfect six-sided prisms.

The remaining grains and scales (0·4741 grm.) had a tin-white colour, and were treated with aqua regia as long as it acted upon them. Three rounded grains remained undissolved in aqua regia, which I suppose were platin-iridium. They weighed 0·0202 grm. =2·2 per cent.

The balance of 0·4539 grm., or 48·4 per cent., was native platinum.

The composition of the sample received from Dr. Charles M. Wetherill was therefore—

New element and gold	not estimated
Sisserskite	=49·4 per cent.
Platin-iridium	2·2 ...
Native platinum.....	48·4 ...

This native platinum is not pure, but contains, like that from other localities, other substances, both alloyed and mechanically mixed with it.

When the 0·4539 grm. was dissolved in aqua regia, 0·0031 grm. or 0·68 per cent. of sisserskite remained undissolved in minute and fine scales.

The solution was evaporated to dryness in a water-bath, dissolved in alcohol, and precipitated with chloride of ammonium. The brick-red double salt thus formed was washed out with alcohol, then dried and powerfully heated. The ignited residue weighed 0·4206 grm. It was treated with weak aqua regia, which left undissolved 0·0110 grm. of iridium and rhodium=2·42 per cent. [This is, of course, only an approximate estimation of iridium, &c.] The presence of rhodium and palladium was also ascertained, but I did not make any quantitative estimations, because the quantity I had to dispose of was too small for the estimation of substances which can be separated only with the greatest difficulty.

The filtrate from the double salts of platinum, &c., precipitated by ammonia, gave 0·0432 grm. of sesquioxide of iron=6·66 per cent. of iron. The composition of this native platinum is therefore—

Platinum (with palladium).....	90·24
Iridium (with rhodium).....	2·42
Iron.....	6·66
Sisserskite	0·68

Silliman's *Journal*, March 1853.

On the Fermentation of Citric Acid. By J. Personne.

The manufacturers of citric acid have long known the difficulty of keeping citrate of lime without its undergoing a change, but the nature of the products of this decomposition have hitherto been unknown. It was known merely that citrate of lime, kept for a certain length of time, would no longer furnish citric acid, and people were satisfied with saying that it was transformed into carbonic acid, or rather carbonate of lime. It is, however, difficult to rest upon this hypothesis, if we consider the formula of citric acid: the spontaneous decomposition of tartar, observed by MM. Noellner and Nicklès, whilst augmenting the doubt as to our knowledge on this subject, serves also to attach a certain interest to the study of this decomposition.

If, after saturating clarified lemon-juice with chalk, the paste of citrate of lime is put into a flask surmounted by a tube fitted for collecting gases, a disengagement of gas will be perceived in a day or two, when the operation is carried on at a temperature of 86° to 95° F., and this continues until the transformation of the citrate is completed. When crude juice is employed instead of clarified, the decomposition proceeds more rapidly, as is shown by the more speedy appearance of the gases.

I have repeated this operation, making use of perfectly pure citric acid, and adding to the paste of citrate of lime a little beer-yeast, and in these circumstances the decomposition proceeds still more rapidly than in the two preceding cases.

In all cases the citrate of lime disappears by little and little; the liquid presents the disagreeable odour of butyric fermentation. The gas was always found to be a mixture of carbonic acid and hydrogen; the quantity of the latter varies continually from the beginning to the end of the operation. The liquid produced by this fermentation, when filtered and evaporated, deposits a white tubercular salt of lime, which presents no indications of crystallization, and dissolves somewhat readily in water, without exhibiting any appearances deserving notice.

This salt, when decomposed by nitrate of silver, gives an abundant white precipitate, which disappears almost completely when washed with hot water. When these washing-waters are carefully evaporated, they furnish a fine acicular crystallization, presenting much resemblance to that of acetate of silver.

That portion of the precipitate remaining after the washing, and the salt obtained crystallized from the water, were examined separately after desiccation over sulphuric acid. The first gave 56·13 per cent. of silver. Three trials of the crystallized salt gave 62·75, 62·60, and 62·86 per cent. of silver. It may be seen that the first of these salts approaches in its composition the butyrate, and the second the acetate of silver. In fact, the butyrate gives in round numbers 54 per cent., and the acetate 64 per cent. of silver. These two salts appear consequently to be mixtures, the one of butyrate of silver with a little acetate, the other of acetate with a little butyrate.

It became interesting to separate these two acids, or to ascertain whether I had not to do with the butyro-acetic acid found by M. Nicklès during the fermentation of tartar*. I endeavoured to effect their separation by fractional distillation. For this purpose, I set a large quantity of citrate of lime in fermentation. When this operation was completed, I transformed the lime-salt which was obtained into a soda-salt by double decomposition with the carbonate of soda. The sodaic solution gave on evaporation an abundant and fine crystallization of acetate of soda; the mother-liquor, when concentrated, furnished a confused mass of crystals, of a fatty appearance, and were moistened with difficulty by cold water.

This mass, reduced to a paste, and treated with syrupy phosphoric acid, soon separated into two layers; the superior, of an oily appearance, resembled a volatile fatty acid, and possessed a mixed odour of acetic and butyric acids. Submitted to distillation, this liquid begins to boil at about 230° F.; the boiling-point then rises by degrees to 320° F., at which it remains nearly stationary. The product obtained at 302° F. possesses the sharp penetrating odour of acetic acid, whilst that which distils over at 320° F. only presents the odour of butyric acid; like that acid, it dissolves in water, the excess swimming on the surface of the aqueous solution.

The solution of this acid, saturated with ammonia and precipitated by nitrate of silver, gave a white flocculent salt, which, when washed and dried over sulphuric acid, furnished on analysis 54·76 and 55·105 per cent. of metallic silver, these numbers agreeing perfectly with that given by calculation for butyrate of silver†. The physical properties of this acid, as well as the simple determination of the silver, might suffice to characterize it very distinctly as butyric acid, and the elementary analysis also confirms this fact‡.

Thus then citric acid, when combined with lime, is changed by true fermentation into *acetic*, *butyric* and *carbonic acids* and *hydrogen*, as indicated by the following equation:—

$$4(C^{12}H^{5}O^{11},3HO)+4HO=3(C^{4}H^{4}O^{4})+2(C^{8}H^{8}O^{4})+20CO^{2}+H^{8}$$

However, the constant presence of hydrogen in the products of the transformation of citric acid may give reason to think that the metamorphosis of this acid is effected at first, so as to furnish lactic acid, according to the formula—

$$4(C^{12}H^{5}O^{11},3HO)+4HO=3(C^{4}H^{4}O^{4})+4(C^{6}H^{6}O^{6})+12CO^{2};$$

and that the lactic acid thus formed is decomposed into butyric and carbonic acids and hydrogen, according to the formula—

$$4(C^{6}H^{6}O^{6})=2(C^{8}H^{8}O^{4})+8CO^{2}+H^{8}.$$

Comptes Rendus, Jan. 24, 1853, p. 197.

* Chem. Gaz., vol. v. p. 58.

† 1. Salt employed, 0·21 grm. Silver obtained, 0·115 = 54·76 per cent.
2. Salt employed, 0·617 grm. Silver obtained, 0·340 = 55·105 per cent.
Calculation gives for butyrate of silver ..... 55·38 per cent.

‡ 1. 0·41 grm. of salt employed gave CO^2 0·364, whence C 24·19 p. c.
2. 0·713 grm. of salt employed gave CO^2 0·634, whence C 24·25 p. c.
HO^2 0·244, whence H 3·80 p. c.

Researches on Stannæthyle. *By* Prof. C. Löwig.

[Continued from p. 132.]

Acetstannæthyle, $Sn^4 Ae^3$.—This radical separates with stannæthyle on the cooling of the alcoholic solution, after the æther has been distilled off (see the investigation of the radicals); it is the essential portion of the mixture of radicals which is first precipitated from the cold alcoholic fluid on the addition of water. It could not be obtained in a pure state, but it possessed the general properties already described. It consists of—

Tin	4 =	236	70·00
Carbon	12	72	22·29
Hydrogen	15	15	7·71

Oxide of Acetstannæthyle, $(Sn^4 Ae^4)O$.—This oxide, like those already described, is precipitated by ammonia from the iodine compound in the form of a white amorphous powder, which is soluble in solution of potash, and in its properties comes nearest to oxide of elaylstannæthyle. Its salts are scarcely soluble in water, but dissolve in alcohol, and also slightly in æther, as is the case with the nitrate. The oxide consists of—

Tin	4 =	236	68·28
Carbon	12	72	21·75
Hydrogen	15	15	4·53
Oxygen	1	8	5·44

Nitrate of the Oxide of Acetstannæthyle, $(Sn^4 Ae^3)O, NO^5$.—This salt is obtained, together with nitrate of elaylstannæthyle, by changing the mixed radicals, which have been precipitated from the cold alcoholic solution by the addition of water, into nitrates by nitrate of silver. As it is very difficult of solution in æther, it can be obtained pure by repeated treatment with cold æther, and recrystallization from the solution in æther and alcohol, from which it is the first to be deposited. This process however is not without difficulty. It is best prepared by exactly decomposing the pure iodide with an alcoholic solution of nitrate of silver. It crystallizes in small, shining, rather hard crystals, which when heated ignite without explosion. Analysis gave—

Tin	..	4 =	236	61·30
Carbon	18·32	12	72	18·70
Hydrogen	4·67	15	15	3·89
Oxygen	..	1	8	2·09
Nitric acid	13·67	1	54	14·02

Iodide of Acetstannæthyle, $(Sn^4 Ae^3)I$.—This compound usually crystallizes from its ætherial solution in remarkably fine needles grouped in a stellate form, but frequently, and especially from its alcoholic solution, in small acicular crystals. It is insoluble in water, but readily soluble in alcohol and æther, although less so than iodide of elaylstannæthyle. It is nearly inodorous. The analyses of this salt have already been given. [Sometimes stellate groups of acicu-

lar crystals, having the appearance of snow, were obtained; but these contained only 24·4 and 23·9 per cent. of iodine, and consequently 4 per cent. less than iodide of acetstannæthyle.]

Bromide of Acetstannæthyle, (Sn^4 Ae^3)Br.—This salt is obtained with bromide of elaylstannæthyle when the ætherial solution of the mixed radicals, which are thrown down from the cold alcoholic solution by water, is saturated with bromine, and the solution left to spontaneous evaporation. The salt separates then first of all in small acicular crystals. It furnished on analysis—

Tin		4 =	236	58·56
Carbon		12	72	17·86
Hydrogen..... ..		15	15	3·73
Bromine	20·50	1	80	19·85

Methstannæthyle, Sn^2 Ae^3.—This radical, next to æthstannæthyle, is the most interesting of the whole group. The last portions which are thrown down by water from the cold alcoholic solution of the mixed radicals consist principally of meth- and æthstannæthyle. This mixture is perfectly colourless, and possesses a spec. grav. of 1·320; it is volatile, and distinguished essentially from those already described by the possession of this property. Methstannæthyle consists of—

Tin.....	2 =	118	56·83
Carbon	12	72	35·12
Hydrogen	15	15	8·05

Oxide of Methstannæthyle, (Sn^2 Ae^3)O.—In order to obtain the pure base, the sulphate is first prepared in the manner already described. This is dissolved in alcohol, the solution mixed with baryta-water, and the whole evaporated to dryness on the water-bath at a temperature of about 176° F. The residue is shaken with anhydrous alcohol, then filtered, and the alcoholic solution evaporated under a bell-glass over sulphuric acid, the air being excluded as completely as possible. At a certain degree of concentration, beautiful, transparent, columnar crystals are formed, which consist of the hydrate of the bases. These crystals fuse at a temperature below 212° F. into an oily fluid, and gradually volatilize, although very slowly, so that the alcoholic solution may be evaporated on the water-bath without an observable loss of the base. The crystals appear to contain water of crystallization as well as hydrate-water. It was not possible to expel this by heat on account of the volatility of the base. If the crystals are fused on the water-bath, and a glass rod moistened with muriatic acid held over the fused mass, white fumes are formed. Placed under a bell-glass over sulphuric acid, the weight of the crystals always diminishes; they do not however lose their transparency, no doubt because both base and water evaporate simultaneously. Upon calcined lime they lose a little of their transparency. The hydrate is difficult of solution in water, but dissolves with tolerable readiness even in hydrated alcohol and in æther. According to the analysis of the salts, the pure oxide consists of—

Sn	2=118	55·40		the hydrate of		
C	12	72	34·27	1 at. oxide of methstannæthyle=	213	35·85
H	15	15	7·04	1 at. water.....	9	4·15
O	1	8	3·29			

Oxide of methstannæthyle approaches the pure alkaline bases in respect of its basic properties. It separates ammonia, magnesia, oxide of zinc, and metallic oxides in general, from their salts. Strongly reddened litmus-paper becomes blue immediately with it; its taste is caustic and penetrating, diffusing itself through the whole throat, and lasting a very long time. In the air it rapidly attracts carbonic acid, which can be again removed from it by quicklime. With acids (except nitric acid), the oxide of methstannæthyle forms salts, which crystallize beautifully, and which all dissolve in alcohol and æther.

Sulphate of the Oxide of Methstannæthyle, $(Sn^2 Ae^3)O, SO^3$, crystallizes from its alcoholic solution in remarkably beautiful columnar crystals, which are not affected by the air; they possess no strong odour, and provoke violent sneezing. The salt is very difficult of solution in water, but dissolves readily in alcohol. The analysis of this salt has already been given.

Nitrate of the Oxide of Methstannæthyle, $(Sn^2 Ae^3)O, NO^5$.—This compound can be prepared directly, and also by the decomposition of the haloid compounds by nitrate of silver. It is obtained directly by adding dilute nitric acid to the alcoholic solution of the base, and then shaking the mixture with æther and a sufficient quantity of water to separate the ætherial solution of the salt. After evaporation, this remains in the form of a syrupy mass, which in the cold forms a colourless, transparent, varnish-like body. The compound is readily soluble in alcohol and æther, and burns without explosion with a dull flame.

For the determination of the nitric acid, the alcoholic solution of the salt was mixed with baryta-water, and the whole evaporated to dryness on the water-bath; the residue was extracted with a mixture of alcohol and æther, the insoluble portion treated with water, and carbonic acid passed into the watery solution, which was then filtered, and the baryta precipitated from the filtrate by sulphuric acid:—

Tin	..	2 =	118	44·18
Carbon.....	..	12	72	26·93
Hydrogen.....	..	18	15	5·62
Oxygen	..	1	8	3·05
Nitric acid	20·60	1	54	20·22

Iodate and Bromate of Methstannæthyle.—If iodine or bromine be added to the alcoholic solution of oxide of methstannæthyle as long as its colour disappears on solution, small shining crystals are deposited, which when heated explode slightly; the solution contains iodide or bromide of stannæthyle.

Iodide of Methstannæthyle, $(Sn^2 Ae^3)I$.—This compound, which is almost always formed simultaneously with iodide of stannæthyle

in the action of iodide of æthyle upon the alloy of tin and sodium, can only be obtained pure by shaking the alcoholic solution of the oxide with watery hydriodic acid, æther, and sufficient water to separate the ætherial solution of the compound. If the ætherial solution is evaporated, the iodide of methstannæthyle remains covered with a thin stratum of water. The latter is removed, and the compound brought into contact with some fragments of chloride of calcium; after some time it is decanted from the chloride of calcium, when the iodide of methstannæthyle appears as a limpid fluid, which strongly refracts light, and possesses a penetrating odour of oil of mustard, which affects the eyes and provokes violent sneezing. Although this compound only boils at from 356° to 392° F., it is nevertheless completely volatilized when left long on the water-bath. Iodide of methstannæthyle mixes with alcohol and æther in all proportions; water dissolves but a small quantity of it, but it dissolves readily in hydrated alcohol. Its spec. grav. is 1·850. It furnished on analysis—

Tin	..	..	..	2	118	35·44
Carbon	21·96	22·06	21·83	12	72	21·68
Hydrogen	4·58	4·68	4·71	15	15	4·26
Iodine	37·93	37·93	37·55	1	127	38·22

Bromide of Methstannæthyle, $(Sn^2 Ae^3)Br$, is obtained by the employment of hydrobromic acid in the same manner as the iodide. The alcoholic solution of the oxide may also be saturated with bromine, the solution then shaken with æther and water, and the ætherial solution evaporated. The bromide exactly resembles the iodide in its physical characters; its spec. grav. is 1·630. Analysis gave—

Tin	..	2	118	41·44
Oxygen	..	12	72	25·26
Hydrogen	..	15	15	5·26
Bromine	27·66	1	80	28·07

Chloride of Methstannæthyle, $(Sn^2 Ae^3)Cl$, is obtained in the same manner as the iodide and bromide. If muriatic acid is added to the alcoholic solution of the sulphate, the chloride is instantaneously formed. It is a limpid, strongly refractive fluid, the odour of which exceeds that of the preceding haloid compounds in intensity. It is the most volatile of all; it mixes with alcohol and æther in all proportions. Its spec. grav. is 1·320. It gave on analysis—

Tin	..	2 =	118·0	49·06
Carbon	..	12	72·0	30·00
Hydrogen	..	15	15·0	6·18
Chlorine	14·55	1	35·5	14·76

Æthstannæthyle, $Sn^4 Ae^5$.—The occurrence and properties of this radical are described above with those of methstannæthyle. Pure æthstannæthyle consists of—

Tin	4 =	236	61·94
Carbon	20	120	31·53
Hydrogen	25	25	6·53

Oxide of Æthstannæthyle, $(Sn^4 Ae^5)O$, is obtained from the pure sulphate in the same manner as the oxide of methstannæthyle from its sulphate. It crystallizes as a hydrate from its alcoholic solution in warty druses. In its properties it agrees with oxide of methstannæthyle; it is a very strong base, renders reddened litmus-paper blue, and has a sharp caustic taste; it separates ammonia and the metallic oxides from their combinations, is difficult of solution in water, but dissolves readily in alcohol and æther; it rapidly attracts carbonic acid from the air, and furnishes with acids crystallizable salts, which are soluble in alcohol. Nevertheless in its basic properties it appears to be somewhat weaker than oxide of methstannæthyle. The free base consists of—

Tin	4 =	236	60·66
Carbon	20	120	30·84
Hydrogen	25	24	6·42
Oxygen	1	8	2·08

The hydrate, which was kept some time in a fluid state on the water-bath, but was not quite free from carbonic acid, gave the following results on analysis :—

Tin	..	4 =	236	56·42
Carbon	28·00	20	120	30·26
Hydrogen	6·41	26	25	6·30
Oxygen	..	2	16	7·02
Oxide of æthstannæthyle		1 =	389	97·73
Water		1	9	2·27

Sulphate of the Oxide of Æthstannæthyle, $(Sn^4 Ae^5)O, SO^3$.—The mode of preparation and the composition of this salt have already been described. It crystallizes from its alcoholic solution in small acicular crystals, which soon lose their transparency when exposed to the air. It is scarcely soluble in water, and dissolves in alcohol with more difficulty than the corresponding salt of methstannæthyle.

Nitrate of the Oxide of Æthstannæthyle, $(Sn^4 Ae^5)O, NO^5$, is obtained in the same manner as the nitrate of the oxide of methstannæthyle, with which it agrees in its properties.

Iodate and Bromate of Æthstannæthyle are separated when the alcoholic solution of the oxide is saturated with iodine or bromine.

The *haloid compounds* of æthstannæthyle differ from those of methstannæthyle only in that they are thickly fluid and possess a lower specific gravity. In odour, in their behaviour with water, alcohol and æther, they agree exactly with the latter. Their mode of preparation is also the same; the alcoholic solution of the oxide is shaken with the corresponding hydracid, æther and water, the ætherial solution evaporated on the water-bath, and the compounds dried over chloride of calcium.

Iodide of Æthstannæthyle, $(Sn^4 Ae^5)I$, is formed simultaneously with the iodide of methstannæthyle during the action of iodide of æthyle upon the alloy of tin and sodium. It is a perfectly colourless, thick, oily fluid, of spec. grav. 1·724. Analysis gave—

Tin	..	..	4 =	236	46·46
Carbon.....	23·74	22·92	20	120	23·62
Hydrogen	5·08	5·21	25	25	4·90
Iodine	25·62	26·43	1	127	25·02

Bromide of Æthstannæthyle, $(Sn^4 Ae^5)Br$.—This is a thinner fluid than the preceding. Its spec. grav. is 1·48. Analysis gave—

Tin	..	4 =	236	51·30
Carbon.....	..	20	120	26·04
Hydrogen.....	..	25	25	5·28
Bromine	17·40	1	80	17·38

Chloride of Æthstannæthyle, $(Sn^4 Ae^5)Cl$, resembles the bromide, and possesses a spec. grav. of 1·30. Analysis gave—

Tin	..	4 =	236·0	56·66
Carbon	..	20	120·0	28·38
Hydrogen	..	25	25·0	6·44
Chlorine.....	8·14	1	35·5	8·62

If potassium or sodium be brought into contact with the haloid compounds, they are immediately reduced. This decomposition affords a means of preparing the pure radicals, and the author has thus obtained a small quantity of methstannæthyle. When the metal has no further action, the radical is extracted from the mass by æther, and the ætherial solution evaporated. With the solid compounds, however, this method gave no favourable result.—*Chem. Pharm. Centralblatt,* Dec. 8, 1852, p. 865.

[To be continued.]

On the Composition of Beet-Root. By A. Robierre.

In the department Loire inférieure the opinion is entertained that the loam-soil of the west is unsuited for the cultivation of Silesian beet. Some persons infer this to be the case from the unsuccessful experiments recently made by sugar manufacturers. Others ascribe the circumstance, that in Brittany beet rich in sugar can only be obtained with difficulty, to the large quantity of chloride of sodium present in the soil of that district. The author has investigated this subject from a technical point of view, and has at the same time endeavoured to ascertain whether, as regards the per-centage of sugar, there is any difference between beet grown upon a soil rich in potash and that grown in the neighbourhood of Valenciennes.

The beet which he procured from the latter locality were of the two kinds which are distinguished in France as varieties,—*collet vert* and *collet rose.* Comparative analyses were made of these and the same kinds of beet from the farm of M. Derrieu near Nantes. Peligot's mode of examination was adopted. 100 parts of beet, in slices cut from various parts of the root, were dried in a water-bath, and extracted with very weak alcohol (1 per cent.). The loss of weight gives the per-centage of sugar. This result is certainly a

little too high, as some minute quantity of a mucilaginous saccharine substance is likewise dissolved. The author considers, however, that this may be disregarded. The albumen and pectine are determined together with the lignine.

The ashes (obtained by calcination in a muffle) from the beet grown on the loamy soils of the Loire inférieure and from the neighbourhood of Valenciennes both contained equal quantities of chlorine. The per-centages of ash were 0·63, 0·70, 0·80. From the results contained in the following table, the author comes to the conclusion, that the Silesian beet may be advantageously cultivated in the Loire inférieure, and further, that the beet grown near Nantes does not contain any substance calculated to render the extraction of the crystallizable sugar difficult.

I. Names of the varieties of beet examined, and their place of growth. II. Time at which they were harvested. III. Quantity of dry substance in 100 parts of beet. IV. Per-centage of water. V. Per-centage of sugar. VI. Per-centage of lignine, albumen and pectine:—

I.	II.	III.	IV.	V.	VI.
Collet rose, Valenciennes.....	End of Sept. 1852.....	13·40	86·60	7·64	5·76
Collet vert, Valenciennes.....	End of Sept. 1852.....	14·60	85·40	7·40	7·20
Collet rose, Nantes	Commencement of Oct.	12·80	87·20	8·24	4·56
Collet vert, Nantes	Commencement of Oct.	10·96	89·04	7·24	3·72
Collet vert, Nantes	November	14·00	86·00	9·32	4·68
Yellow German beet.....	November	13·07	86·30	10·05	3·65
Common beet	November	11·05	88·05		
Silesian beet, gr. near Nantes	October	14·00	86·00	5·00	9·00

Comptes Rendus, xxxvi.

On an apparently new Mode of Formation of Sebacic Acid, and on the Constitution of the Acids of the Group $(C^n H^{n-2}) + O^8$. *By* Dr. Rudolph Wagner.

Sebacic acid (sebacylic acid, pyroleic acid) has hitherto been found, together with caproic acid and caprylic acid (and perhaps also capric acid), amongst the products of the distillation of oleic acid and similar fats. It has also recently been prepared by the saponification of the amide of ricinoleic acid by means of potash. The apparent mode of formation hereafter described may perhaps throw some light upon the constitution of the fatty acids.

Sebacic acid belongs, according to Gerhardt, to the series of homologous acids, which are composed according to the formula $(C^n H^{n-2}) + O^8$, to which also suberic, pimelic, adipic, and succinic acids belong. This group has been with reason called the succinic acid group.

By the treatment of butyric acid with nitric acid, Dessaignes obtained succinic acid, $C^8 H^8 O^4 + 6O = C^8 H^6 O^8 + 2HO$.

As the 8 atoms of carbon of the butyric acid reappear in the succinic acid, capric acid, $C^{20} H^{20} O^4$, which is homologous with butyric acid, should, if we may judge from analogy, furnish sebacic

acid, $C^{20}H^{18}O^8$, which is homologous with succinic acid, and which stands in the same relation to capric acid as adipic to caproic acid, pimelic to œnanthic acid, and suberic to caprylic acid.

The author has endeavoured to convert capric acid into sebacic acid. The first substance which he employed was the aldehyde of capric acid, or oil of rue*.

Common oil of rue was heated in a retort with three or four times its quantity of dilute nitric acid over a slack fire until the commencement of ebullition. The boiling was continued several days, and the fluid which passed over poured back into the retort from time to time, with the occasional addition of some nitric acid. The action of the acid upon the oil of rue was so regulated that but little reddish vapour appeared in the neck of the retort. After the heating had been continued several days, two strata of fluid were found in the retort; the upper, which was brownish, consisted of oxidized, and partially also of unchanged oil; the lower, yellowish, nitric stratum, had deposited a large quantity of white flakes. The two fluids were separated by means of a pipette, and the lower evaporated on the water-bath to a small volume. The odour evolved during the evaporation resembled that of the higher members of the series of volatile fatty acids. The alcoholic solution of the upper layer presented after a few days the characteristic odour of pelargonate of oxide of æthyle. The residue of the evaporation of the lower layer appeared on cooling as a fat-like white mass; it was again dissolved in boiling water. The pure substance separated from the water, after it had been pressed between blotting-paper and dried, had the following properties:—

It appeared in white laminæ, fused when carefully heated on platinum foil, and sublimed when more strongly heated. The fumes provoked coughing. In consequence of the small quantity of this substance which the author had at his command, he was unable to purify it completely, and free it from a nitrogenous product.

The substance was dissolved in alcohol, and the alcoholic solution precipitated with a solution of neutral acetate of lead, also in alcohol. The resulting white flocculent precipitate was collected on a filter, washed with alcohol, and the quantity of lead contained in the lead salt thus obtained determined in the usual manner. The salt contained 54·84 of oxide of lead. Sebate of lead, $C^{20}H^{16}O^6$, 2PbO, requires 55·02 per cent. of oxide of lead.

From this it is not improbable that the acid obtained by the treatment of oil of rue with nitric acid may be sebacic acid. The formation of sebacic acid from the oil of rue might be expressed in the following manner:—$C^{20}H^{20}O^2$, oil of rue $+O^8=C^{20}H^{18}O^8$, sebacic acid $+2HO$; also $C^{20}H^{20}O^2$, oil of rue $+O^2=C^{20}H^{20}O^4$, capric acid; and $C^{20}H^{20}O^4$, capric acid $+O^6=C^{20}H^{18}O^8$, sebacic acid $+2HO$.

As collateral products, pelargonic acid, and probably also some suberic acid, make their appearance. In the same manner, lipic

* Chem. Gaz., vol. vii. p. 175.

(pyrotartaric) acid may be obtained from valerianic acid, adipic from caproic acid, suberic from caprylic acid, and pimelic from œnanthylic acid.

According to the most recent investigations of Dessaignes, an acid which crystallizes in beautiful rhombic prisms is formed by the continued action of nitric acid upon valerianic acid; according to Dessaignes, this is either $C^{10} H^9 (NO^4) O^4$=nitrovalerianic acid, or $C^{10} H^7 (NO^4) O^4$=nitroangelicic acid. It appears to the author that the more probable supposition is, that this acid is derived from lipic acid, $C^{10} H^8 O^8$*.

It appears from what has been stated above, that a connexion exists between the two homologous series represented by $(2C^n H^n) + 4O$ and $(2C^n H^{n-2}) + O^8$, which has become more evident since Gerhardt has succeeded by treating members of the group $(2C^n H^{n-2}) + O^8$ with fused hydrate of potash, in converting them into acids of the formula $(2C^n H^n) + 4O$.

The following table shows the connexion between the members of the two groups:—

A. Treatment with nitric acid produces from—

Butyric acid	$C^8 H^8 O^4$,	succinic acid.....	$C^8 H^6 O^8$
Valerianic acid....	$C^{10} H^{10} O^4$,	lipic acid	$C^{10} H^8 O^8$
Caproic acid.....	$C^{12} H^{12} O^4$,	adipic acid	$C^{12} H^{10} O^8$
Œnanthic acid....	$C^{14} H^{14} O^4$,	pimelic acid	$C^{14} H^{12} O^8$
Caprylic acid	$C^{16} H^{16} O^4$,	suberic acid.....	$C^{16} H^{14} O^8$
Capric acid	$C^{20} H^{20} O^4$,	sebacic acid.....	$C^{20} H^{18} O^8$

B. Treatment with hydrate of potash produces from—

Succinic acid	$C^8 H^6 O^8$,	propionic acid	$C^6 H^6 O^4$
Lipic acid.....	$C^{10} H^8 O^8$,	butyric acid.....	$C^8 H^8 O^4$
Adipic acid	$C^{12} H^{10} O^8$,	valerianic acid....	$C^{10} H^{10} O^4$
Pimelic acid	$C^{14} H^{12} O^8$,	caproic acid.....	$C^{12} H^{12} O^4$
Suberic acid	$C^{16} H^{14} O^8$,	œnanthylic acid ..	$C^{14} H^{14} O^4$
Sebacic acid.....	$C^{20} H^{18} O^8$,	pelargonic acid....	$C^{18} H^{18} O^4$

Oxalic acid, when treated with fused hydrate of potash, gives formic acid (Pelouze and Millon), consequently the first member of a series of acids which are produced from the acids of the succinic acid group by treatment with potash. This is also a new reason for referring oxalic acid, with Gerhardt, to the bibasic acids, and regarding it as the first member of the succinic acid group; for if succinic acid be $C^8 H^6 O^8$, oxalic is $C^4 H^2 O^8 = 2(C^2 O^3, HO)$. The latter would then, by proper treatment with nitric acid, furnish acetic acid.

In the succinic acid group, the member with the formula $C^5 H^4 O^8$, lying between the oxalic and succinic acids, has hitherto been wanting, as well as that lying between the suberic and sebacic acids with the formula $C^{18} H^{16} O^8$. As regards the former, there has

* See Chiozza "On a Combination of Pelargonic Acid with Deutoxide of Nitrogen," Chem. Gaz., p. 123 of our present volume.

been known since the year 1845 an acid of the composition $C^6H^4O^8$, which is sufficiently worthy of the attention of chemists. This is the nicotic acid discovered by Barral in the leaves of tobacco, which stands in the same relation to propionic acid as oxalic acid to acetic acid. According to Barral, it furnished carbonic and acetic acids by dry distillation; according to Gerhardt's views, this acid would furnish the same substances by treatment with hydrate of potash. It appears therefore as though the nicotic acid, which according to Barral is a bibasic acid $=C^6H^2O^6, 2HO$, may really be homologous with the members of the succinic acid group. With regard to the second of the acids wanting in the group, it is possible that it may be prepared by the carefully-managed action of nitric acid upon pelargonic acid.

If oxalic acid be assumed as the first member of the succinic acid group, its members may be regarded as oxalic acid (bibasic) in which 1 equiv. of hydrogen is replaced by 1 equiv. of the radicals of the alcohols.—*Centralblatt*, Feb. 9, 1853, p. 89.

PROCEEDINGS OF SOCIETIES.

Institution of Civil Engineers.

March 1st, 1853.

"On the increased Strength of Cast Iron, produced by the use of improved Coke," by Mr. W. Fairbairn, M. Inst. C.E.

The object of this communication was chiefly to point out what were believed to be the causes of the inferiority of iron, in many works, apart from the varying qualities of the ores. These were stated to be the introduction and application of the hot blast, which had enabled the iron-master to reduce into cast and malleable iron a very large per-centage of cinders, slag, and other impurities, containing large proportions of silicate of iron, sulphur and phosphorus, all of which tended to destroy the tenacity of the metal, and to render it either "red short" or "cold short." Sufficient attention was not devoted by those who were entrusted with the regulation and charging of the blast-furnaces, to the chemical composition of the ironstone, by which the relative proportions of the flux and fuel employed in its reduction should be regulated. The chemical composition of the limestone or the coal was not sufficiently known, these materials often varying in quality as much as the ironstone itself; and the iron-smelter was unable to tell with certainty the quality of iron which his furnace would produce. Instances had occurred where a siliceous ore had been used for three or four hours successively, and then at once it had been replaced by an aluminous, and sometimes by a calcareous ironstone, without the change being made in the proportions of limestone or coal, which was evidently required by the different qualities of those ores.

The following analysis exhibited the different quantities of silicium existing in cast iron:—

White crude.	Monkland.	Coltness.	Eglinton.	Dalmellington.
0·18	1·53	2·69	3·12	4·42

The injurious action which an impure fuel had upon the quality of the iron was particularly alluded to; and the necessity of removing the sulphur from the coal or coke, when employed in the blast-furnaces, before it could be imparted to the cast iron during the process of smelting, was strongly enforced. The difference in the quality of iron smelted with coal, and by the application of a process which had been recently introduced by Mr. Crace-Calvert, compared with iron smelted in the ordinary way, was exhibited in the following analysis:—

Proportions of Sulphur.

Eglinton pig iron.	Melted in the cupola with ordinary coke.	Melted with improved coke.
0·336	0·281	0·191

The following table showed the improved quality of iron after the application of the chloride of sodium in the blast-furnace, by which the proportion of sulphur had been diminished:—

Monkland without chloride.	Monkland with chloride.	Dalmellington without chloride.	Dalmellington with chloride.
0·390	0·150	0·956	0·218

And the increased bearing weight of one-inch bars, cast from these irons:—

579°	627°	487°	556°
576°	655°	456°	525°
		487°	544°
		470°	562°
			569°

These improvements were described to have been effected at a very small cost by the following simple process:—If the blast-furnace was worked entirely with coal, chloride of sodium was added with each charge in proportion to the quality of the ore and flux employed; but a better result was produced if the coal was previously converted into coke, and an excess of the chloride was used in its preparation, in order to act on the sulphur of the coal and of the ore, should any be found therein; and a greater improvement was manifested in the quality of the iron when only coke so prepared was used in the blast-furnace. The coke so purified emitted no sulphurous fumes when taken out of the coke-oven; nor, when extinguished with water, did it give off the unpleasant odour of sulphuretted hydrogen; nor was there any sulphurous acid gas liberated during the operation of smelting iron in the cupola, or in raising steam in the locomotive boiler by coke so prepared; and it

was stated that these decided advantages were gained, in some cases, at an additional cost of only one penny per ton of fuel.

The chemical action of the chloride of sodium was thus described:—When coal was first subjected to heat in a coke-oven, the bisulphuret of iron contained in the coal was decomposed into sulphur, which was distilled or burned, and also into protosulphuret of iron, which remained in the mass, and was acted upon by the chloride of sodium, as it was volatilized at a red heat. Thus chloride of iron and protosulphuret of sodium were produced. Then a second chemical reaction ensued. The protochloride of iron was decomposed into a subperchloride of iron, and the chlorine gas thus liberated reacted on the sulphuret of sodium, giving rise to chloride of sodium and to chloride of sulphur, which latter was disengaged; so that the prepared coke contained less sulphur than the ordinary coke. But admitting even that a small portion remained, it would be in the state of sulphuret of sodium, which would not yield any of its sulphur during combustion, but would pass into the cinders of the blast-furnace or of the cupola, and into the ashes of the fire-box in the locomotive, thus preventing the injurious effects of the sulphur on the fire-bars and the copper of the fire-box, and on the brass tubes of the boiler of the locomotive; and the sulphur thus fixed did not enter into combination with the iron, preventing crystallization during the process of smelting, and giving greater tenacity and closeness of texture both to the cast and malleable iron.

The second part of the paper gave the results of a series of experiments which had been made by Mr. Fairbairn upon trial bars one inch square, cast from iron melted in the cupola with coke prepared by the process of Mr. Crace-Calvert. Specimens of the iron so prepared were exhibited, when the closeness of texture and the absence of the "honey-comb" appearance, prevailing in the iron cast with the ordinary coke, was clearly demonstrated. The mode of experimenting was described, and the results were given very elaborately, and it was shown that the average increase of strength was from 10 to 20 per cent.

Taking the mean of the whole experiments, the following conclusions were arrived at:—

	lbs.
The mean breaking weight of the bars per square inch, melted with the improved coke, was	515·5
Ditto ditto with ordinary coke	427·0
	=88·5

in favour of the castings produced from the improved coke, or in the ratio of 5 : 4.

The experiments on the bars smelted with the improved coke indicated iron of a high order as to strength, and might be considered equal to the strongest cold-blast iron. The metal appeared to have run exceedingly close, and exhibited a compact granulated structure, with a light gray colour.

THE CHEMICAL GAZETTE.

No. CCLIII.—May 2, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Quinidine. *By* H. G. Leers.

Quinidine, which was discovered by Winckler, exists with a little quinine in the *Cinchona bogota**. In this bark the author found from 2·61 to 2·66 per cent. of quinidine. In his investigations he employed commercial quinidine from the manufactory of Dr. Zimmer of Frankfort, which he purified from a small quantity of quinine by recrystallization.

1 part of quinidine is soluble in 2580 parts of water at 51° F., in 1858 parts at 212° F.; at 51° F., 100 parts of æther dissolve 0·70 of quinidine. At the same temperature, 12 parts of alcohol of spec. grav. 0·835 dissolve 1 part of quinidine. Quinidine crystallizes from alcohol of spec. grav. 0·833 in colourless, glassy, hard prisms, with angles of 86° and 94°; the surfaces of the prisms are strongly striated; the same striation is exhibited on the truncated surfaces of the more obtuse angles; cleavage very perfect in the direction of the latter surfaces. If the crystals be heated in a platinum crucible over the spirit-lamp, they retain their lustre and form at first, and only fuse at 347° F., when, without decomposition or loss of water, they fuse into a clear, wine-yellow fluid, which on cooling forms a grayish-white crystalline mass. If the heat be raised above 347° F., the yellow fluid ignites, and burns with a red, flashing, very smoky flame, evolving an odour like quinoyle and oil of bitter almonds, and leaving behind a voluminous, readily combustible cinder. The taste of quinidine is less strongly bitter than that of quinine.

By the distillation of quinidine with hydrate of potash and a little water, a yellow oleaginous substance is obtained, which possesses an alkaline reaction and all the properties of quinoline. If pure quinidine be finely powdered and brought into contact with chlorine-water, it dissolves therein without any remarkable appearance; quinine and cinchonine act in the same manner with liquid chlorine. If ammonia be added to these solutions, the cinchonine is precipitated from its solution as a white powder, the solution of quinine acquires a grass-green colour, whilst the solution of quinidine remains unchanged. The reaction with quinine is rendered still more sensible by æther, that is to say, if the substance to be tested for quinine be first finely powdered, agitated with æther, and liquid chlorine and ammonia be then added to the solution, the fluid will become of a green colour with the least trace of quinine.

* Chem. Gaz., vol. vi. p. 164.

Most of the salts of quinidine dissolve more readily in water than those of quinine. They are readily soluble in alcohol, but are not soluble in æther. The watery solutions of neutral and acid salts of quinidine give, with potash, soda, ammonia, and the carbonates and bicarbonates of the alkalies, white, pulverulent precipitates, which appear crystalline after long standing, and are not soluble in an excess of the precipitant. Phosphate of soda, bichloride of mercury, and nitrate of silver give white precipitates. Chloride of gold gives a pale yellow, chloride of platinum an orange-yellow, and protochloride of palladium a brown precipitate. Sulphocyanate of ammonia produces a white, and tannic acid a dingy yellow precipitate with the salts of quinidine. The analysis of quinidine, dried at 230°, gave—

Carbon	76·66	36	= 216	76·59
Hydrogen.....	7·74	22	22	7·80
Nitrogen	9·99	2	28	9·93
Oxygen	..	2	16	5·68

Neutral Sulphate of Quinidine, $C^{36}H^{22}N^{2}O^{2}, SO^{3}HO$, is prepared by neutralizing quinidine with dilute sulphuric acid. It forms stellate, silky, acicular crystals, soluble in 130 parts of water at 51° F., in 16 parts at 212° F. It is readily soluble in alcohol, but difficult of solution in æther. Analysis of the salt, dried at 212° F., gave—

Carbon	64·70	54·79	36	= 65·25
Hydrogen	7·18	6·91	23	6·95
Sulphuric acid ..	11·99	12·08	1	12·08

The following salts were prepared in a similar manner to the preceding; twice as much acid is employed to form the acid salts as for the neutral ones.

Acid Sulphate of Quinidine.—The solution is dried *in vacuo* over sulphuric acid. When the solution had acquired a syrupy consistence and a strong brown colour, a crystalline mass of rather strong, shining, asbestos-like needles of a pale yellow colour was formed. The crystals separated from the mother-liquor were washed with a mixture of alcohol and æther, and pressed between blotting-paper. The salt showed a considerable difference in the quantity of sulphuric acid contained in it, and consequently still contained some neutral sulphate of quinidine.

Neutral Muriate of Quinidine, $C^{36}H^{22}N^{2}O^{2}, HCl, 2HO$, was obtained by spontaneous evaporation in large, glassy, rhombic prisms. 1 part of the salt required 27 parts of water for its solution; it is very readily soluble in alcohol, but scarcely at all in æther. Analysis of the salt, dried at 212° F., gave—

Carbon	64·57	64·11	36	= 64·19
Hydrogen	7·28	7·06	25	7·13
Chlorine.....	9·95	10·16	1	10·54

Acid Muriate of Quinidine, $C^{36}H^{22}N^{2}O^{2}, 2HCl, 2HO$.—The solution furnished by spontaneous evaporation fine large crystals of a yellow colour. The acid muriate of quinidine, completely dried

over sulphuric acid, lost 5·8 per cent. of water at 212° F. It is very soluble in water and alcohol. Analysis of the salt, dried at 212°, gave—

Carbon	58·30	..	36	= 57·93
Hydrogen	7·12	..	26	6·97
Chlorine.....	18·96	19·00	2	18·99

Platino-chloride of Quinidine, $C^{36}H^{22}N^{2}O^{2}$, 2HCl, $2PtCl^{2}+4HO$, is an orange-yellow precipitate, which, when dried at 230° F., contains 27·11 per cent. of platinum; calculation gives 27·04.

Hydrargyro-chloride of Quinidine, $C^{36}H^{22}N^{2}O^{2}$, 2HCl, 2HgCl. —This is produced from the solution of the base in alcohol of spec. grav. 0·848, to which a little muriatic acid has been added, by the addition of an equivalent of perchloride of mercury dissolved in alcohol. It separates in small scaly crystals of a pearly lustre, which are very difficult of solution in cold water. The crystals, dried over sulphuric acid, lose no water at 230° F. Analysis:—

Carbon	34·77	..	36	= 34·52
Hydrogen	4·01	..	24	3·83
Mercury	31·98	31·91	2	31·97
Chlorine.....	22·60	22·31	4	22·63

Nitrate of Quinidine crystallizes from its solution, standing over sulphuric acid, in fine, large, tubercular crusts of an enamel-like appearance. If the mother-liquor be allowed to evaporate still further, there is formed on its upper surface a hemispherical, white, wax-like mass, whilst the fluid acquires a somewhat greenish colour. It is readily soluble in water.

Chlorate of Quinidine, obtained by the mutual decomposition of neutral sulphate of quinidine and chlorate of potash, and recrystallization from alcohol of spec. grav. 0·833, forms long, white, silky prisms, grouped in tufts. It fuses at a gentle heat into a transparent mass, and explodes very violently when the heat is somewhat raised.

Hyposulphite of Quinidine, obtained by the decomposition of neutral sulphate of quinidine with hyposulphite of soda, appears in long fine needles of an asbestos-like appearance. It is rather difficult of solution in water, but dissolves readily in alcohol.

Fluate of Quinidine.—The solution furnished by spontaneous evaporation a mass of white, crystalline, silky needles, which are very readily soluble in water. On the addition of chloride of calcium, a precipitate is formed, which does not dissolve in acetic acid.

Acetate of Quinidine forms fine, long, silky needles, which are very difficult of solution in cold water. During drying, the salt very readily loses a portion of its acid.

After the removal of the crystals, the mother-liquor furnishes by spontaneous evaporation another salt, which forms a mass of small acute needles, of a porcellanous appearance, which are grouped together in a hemispherical form. This salt is much more soluble in water than the preceding.

Oxalate of Quinidine separates, after the cooling of a hot alcoholic solution of quinidine which has been neutralized with oxalic

acid dissolved in alcohol, in the form of long, white, silky needles, which are very difficult of solution in water. If the mother-liquor be left to evaporate spontaneously, a salt crystallizes from it in tubercular crusts of a dull white appearance: this is rather more soluble in water than the former.

Tartrate of Quinidine.—Tartaric acid forms two different salts with quinidine. When this acid is saturated with quinidine at a boiling heat, a salt separates on the cooling of the acid solution in small acicular crystals of a pearly lustre, which are very difficult of solution in water. If the solution of neutral tartrate of quinidine be left to evaporate spontaneously, a salt is obtained in beautiful glassy needles; further evaporation of the mother-liquor gives small, white, dull, hemispherical crusts of little needles.

Citrate of Quinidine, obtained by the saturation of pure quinidine with pure citric acid at a boiling heat, crystallizes from the solution, on its cooling, in small needles of but little lustre. The salt is difficult of solution in water.

Formiate of Quinidine crystallizes in long silky needles. It is tolerably easy of solution in water.

Butyrate of Quinidine crystallizes from the neutral solution in large tubercular crusts of a porcellanous appearance. The salt is readily soluble, and has a strong odour of butyric acid.

Valerianate of Quinidine is deposited during spontaneous evaporation in tubercular crusts, which have in their centre a paler nucleus of a radiate structure. The salts smell strongly of valerianic acid. If the solution of valerianate of quinidine be evaporated on the water-bath, the fluid acquires a brown colour, with separation of oleaginous drops and diffusion of a penetrating odour of valerianic acid.

Kinate of Quinidine is obtained from the neutral solution by spontaneous evaporation as a white silky mass of small needles. It is readily soluble in water and alcohol.

Hippurate of Quinidine.—Hippuric acid dissolved in water was saturated whilst hot with quinidine. On cooling, the salt crystallized from the solution in long silky crystals, which had the appearance and form of fern leaves. It is readily soluble in water and alcohol.

According to the preceding analytical results, quinidine is distinguished from cinchonine by containing 2 atoms less carbon, as follows:—

Quinidine.....	$C^{36}\ H^{22}\ N^2\ O^2$ (Leers).
Quinine	$C^{38}\ H^{22}\ N^2\ O^4$ (Laurent).
	$C^{20}\ H^{12}\ N^2\ O^2$ (Liebig).
Cinchonine	$C^{38}\ H^{22}\ N^2\ O^2$ (Laurent).
	$C^{20}\ H^2\ N\ O$ (Liebig).

Ann. der Chem. und Pharm., lxxxii. p. 147.

On the Composition of Milk.

By MM. Vernois *and* Alfred Becquerel.

Previous analyses of the milk of women, cows, asses, &c., have given such widely different results, that the discrepancies would

appear to be owing more to the methods of analyses than to any real difference of composition. The authors have therefore, in their analyses of milk from various animals in healthy and diseased states, adopted the following process, based upon our existing knowledge of the behaviour of the constituents of milk.

60 grms. of milk are divided into two equal parts, one of which is evaporated to dryness at 140° or 176° F. The weight of the residue gives the per-centage of water and of solid constituents. This residue is then extracted with æther; the ætherial solution gives on evaporation the butyraceous substances, which are weighed. There then remain to be determined caseine, sugar, extractive matter and the salts. The latter are obtained by calcining the substance which has been treated with æther.

The remaining constituents are to be determined in the other half of the milk. The caseine is coagulated by the addition of rennet and acetic acid, and the sugar determined in the filtered liquid by means of the polarization saccharometer. The per-centage of caseine is found by deducting the weight of all the other constituents from the total weight of the milk. The result thus obtained is certainly above the truth, and corresponds to caseine + extractive; but considering the indefinite nature of the latter, the authors are of opinion that this circumstance may be overlooked.

A great number of analyses have been made in this way by the authors. From eighty-nine analyses of milk from women of ages varying from 15 to 45 years, and in various states of health, they infer that the composition of normal human milk is—

Water			889·08
Solid constituents	Sugar	43·64	110·92
	Caseine and extractive	39·24	
	Butter	26·66	
	Salts (ash)	1·38	
			1000·00
Specific gravity			1032·67

The milk of women from 15 to 20 years of age contains more solid constituents than that of those between 30 and 40. In colostrum the quantity of butter is sensibly larger. In persons of weak constitution, the composition of the milk remains almost normal; in those of stronger constitution, the quantity of fixed constituents decreases. The milk of women with dark hair is better than that of those with light hair. With a spare diet the milk becomes watery, and deficient especially in caseine and butter.

The second part of the authors' investigations referred to the milk of diseased women. They made forty-six analyses, nineteen of which were of milk from women suffering under acute, and twenty-seven from women suffering under chronic affections. They found that the composition of the milk sufficiently justified such a classification. In both conditions, indeed, the per-centage of water is smaller, that of the solid constituents larger, than in normal milk. In acute affections the per-centage of sugar is smaller, while those of the other constituents from the salts to caseine are progressively

larger, the increase in the latter alone being almost equivalent to the decrease in sugar. In chronic affections the per-centages of butter and salts are larger, that of sugar normal, that of caseine deficient. Thus while in acute affections there is a deficiency of respiration constituents and an excess of plastic constituents, the reverse obtains in chronic affections. The following table shows the composition of milk from subjects in these states:—

Milk.		In acute affections.		In chronic affections.	
Water		884·91		885·80	
Solid constituents	Sugar	33·10	115·09	43·37	114·50
	Caseine and extractive	50·40		37·06	
	Butter	29·86		32·57	
	Salts (ash)	1·73		1·50	
		1000·00		1000·00	
Specific gravity		1031·20		1031·47	

The most important results obtained by the authors are, that in tubercular disease of the lungs, unaccompanied by diarrhœa and atrophy, there is no perceptible alteration in the milk. In the opposite case, however, the total quantity of solid constituents is much smaller, the deficiency being in the butter only. In syphilis the specific gravity is very high, the per-centage of butter small, that of the salts very high. The authors consider that it is impossible to decide as to the quality of milk from the determination of one constituent, but that a complete analysis must be made.—*Comptes Rendus*, January 24, 1853.

On Glass containing Gold. By M. Splittgerber.

With regard to the red and colourless glasses containing gold, H. Rose has expressed an opinion that the gold is contained in the latter as a silicate of the protoxide*. When such a colourless acid or neutral silicate is again heated to a temperature below that at which glass melts, some protoxide separates, and this communicates to the glass a fine ruby-red colour.

Splittgerber, on the other hand, is still of the opinion formerly expressed by him, that in the coloured glass the gold is in a lower stage of oxidation than in the colourless, because according to his experiments the coloured glass only becomes colourless by taking up oxygen. By repeated investigations, the author always found that glass which was blown colourless becomes red again by being heated; from which it follows, that the gold does not nearly all separate in the metallic state, as perhaps might have been supposed. The synthetic mode of clearing up the question is the only available method, the analytical mode not being applicable.

Moreover, the employment of the microscope in this case gives no further explanation, for even with the highest powers the colouring matter was not resolved into individual portions, and this takes place only when the reduced gold has become collected into larger particles; but then the glass is decolorized.

* Chem. Gaz., vol. vi. p. 51.

In any case it is worthy of remark, that after the auriferous glass is formed, the colour does not depend so much upon a determinate degree of heat, as upon this temperature being attained by gradual elevation from a lower degree, by which alone the necessary impulse to decomposition and separation is given; whilst this phænomenon does not occur on cooling to the same temperature; otherwise the preparation of the colourless gold-glass would be impossible.

The author has instituted the following experiments. They were made in a Sefström's furnace:—

I. 100·0 parts sand,
66·0 parts soda,
10·0 parts chalk,
1·5 part purple of Cassius,

were fused in an hour into a good white glass, which had only the usual greenish tinge of soda glass, and there was in it besides the gold only the tin of the purple of Cassius. A portion of it held in the fire on an iron rod became as it fused dark yellow and dull by reflected, but of a beautiful lilac colour by transmitted light, in consequence of the reduced gold in it. Before the blowpipe it immediately became reddish, but not intensely so; but even after long blowing no gold separated. Heated to redness in a platinum crucible, the colourless glass became first reddish, but the colour then passed rapidly into orange. This was the first specimen of gold glass which the author prepared with soda, he having always previously made it with potash. It is not a fine ruby-coloured glass. Its spec. grav. was 2·462 at 53° F., and this, as well as its absolute weight, did not change in the least in the platinum crucible.

II. 100·0 parts sand,
50·0 parts soda,
12·5 parts chalk,
4·0 parts purple of Cassius,

fused rapidly into a glass, which however did not become quite clear; on pouring it out of the crucible, it tarnished slightly, whilst thin threads of glass remained colourless, which perhaps arises from the fact, that thick masses, after they have cooled externally, receive a sudden amount of heat from within. Before the blowpipe this glass became more intensely coloured than the preceding, with which otherwise it exactly agreed; nevertheless there were many grains of reduced gold separated in the melting pot.

In order now to observe the behaviour of gold alone in the glass, the author dissolved some gold in nitromuriatic acid, mixed it with the sand, allowed it to dry, and then mixed it intimately with the other ingredients.

III. 100·00 parts sand,
62·50 parts soda,
12·50 parts chalk,
0·75 part gold.

This fusion was accidentally hurried, which produced a bad glass, containing many undissolved portions. The glass, when poured out, had a slight reddish tinge; that remaining in the melting pot, when again heated, became rose-coloured, and had grains of gold at its bottom. The glass first poured out only acquired a rose colour with difficulty before the blowpipe; this perhaps arose from the small quantity of gold contained in it. Heated in a platinum crucible for ten minutes over the spirit-lamp, the fragments of glass became rose-red. The author repeated this experiment with the addition of a little more gold.

IV. 100·0 parts sand,
62·5 parts soda,
12·5 parts chalk,
1·3 part gold.

After an hour's fusion, the glass was obtained quite good and colourless; there was however a good deal of gold separated in a metallic form in the melting pot. It only acquired colour after it had been long fused before the blowpipe, then appearing liver-coloured and dull by reflected, and rose-coloured and bluish by transmitted light, evidently caused by the tendency of the gold to separate in a metallic form, which was not the case to the same extent with the glass to which purple of Cassius had been added. Heated in a platinum crucible, it acquired a fine carmine-red colour. At 59° F. the spec. grav. of this glass was 2·444, which, like the absolute weight, was not in the least altered during the change of colour. The two following experiments were performed with pearl-ash, for comparison with the preceding in which soda was employed.

V. 100·0 parts sand,
62·5 parts pearlash,
25·0 parts chalk,
2·5 parts purple of Cassius.

After one hour's fusion a tolerably good, but rather bubbly glass was obtained. As it was very difficult of fusion, it would not flow out of the melting pot, but was taken out in portions by a pair of tongs; it was completely colourless, whilst the glass which remained in the melting pot, and which had cooled with it, had become of a topaz-yellow colour, and some grains of gold had separated at the bottom. During fusion the mass had evolved fumes, which proceeded from the salts which contaminated the pearlash; a considerable deduction must therefore be made from the pearlash employed, which explains the difficulty of fusion. The colourless glass acquired before the blowpipe a rather fine ruby-red colour; when heated in a platinum crucible, it became first topaz-yellow, and afterwards ruby-red. Its spec. grav. was 2·466 at 61° F.

VI. 100·0 parts sand,
62·5 parts pearlash,
25·0 parts chalk,
1·3 part gold dissolved in nitromuriatic acid.

In this melting, so much gold was separated in the metallic state, that perhaps scarcely 20 per cent. of the quantity employed remained in the glass, which consequently, when heated, only acquired a faint violet colour with difficulty, and exhibited reduced gold. Its spec. grav. was 2·460.

From this and previous investigations of the author, it appears that it is not advisable to employ gold alone without another metallic oxide, as it is too readily reduced again to the metallic state; in manufactories glass containing lead is alone applied to this purpose.

The two following meltings show the behaviour of platinum in glass fluxes:—

100·00 parts sand,
50·00 parts soda,
10·00 parts chalk,
1·01 part platinum diss. in nitromuriatic acid.

This mixture fused into a good glass, which however was coloured quite uniformly of a mouse-gray by the reduced platinum, in such a manner that even with a thickness of an eighth of an inch the window bars could be seen through it.

In order if possible to obtain the platinum in the oxidized state, the author now tried the following composition:—

100·0 parts sand,
100·0 parts minium,
20·0 parts nitrate of potash,
20·0 parts potash,
0·4 part platinum;

but this also gave only a grayish turbid glass, which had strongly attacked the melting pot.—Poggendorff's *Annalen*, lxxxv. p. 504.

On the Presence of Alumina in Boghead Coal, and on the Employment of the Ashes of the latter in the Manufacture of Alum. By* Thornton J. Herapath.

A short time ago, a gentleman placed in my father's hands for analysis some specimens of Retinasphalt and of Boghead coal; and intimated that he wished to know whether either of these minerals contained potash or alumina, as he had been given to understand that they had been largely employed of late by certain gas companies, which he named, as substitutes for coal in the preparation of gas, and that alum had been manufactured from their ashes.

The specimens forwarded to us were submitted to analysis with the following results:—

The Retinasphalt yielded on incineration 5·53 per cent. of ash, and was found to contain only traces of alumina and no potash. Two specimens of Boghead coal furnished respectively (No. 1) 20·56 and (No. 2) 24·09 per cent. of ash. The ash of No. 1, when treated with strong hydrochloric acid, yielded a solution from which 6 grs. of alumina were precipitated on the addition of ammonia; No. 2

* Communicated by the Author; having been read before the Bristol Philosophical Society on March 31st.

yielded 7·12 grs. of alumina. Consequently the ashes of these two specimens contained respectively 29·18 and 29·55 per cent. of alumina soluble in acids:—

Specimen.	Ash per ton of coal.	of alumina.	of crystallized potash alum.
	about	about	
No. 1.	460½ lbs., containing	134½ lbs.,	equal to about 11 cwt. 1 qr. 12 lbs.
No. 2.	539½ lbs., containing	159½ lbs.,	equal to about 13 cwt. 1 qr. 24 lbs.

Specimen.	Alumina per ton of ash.	Crystallized potash alum.
No. 1.	About 5 cwt. 3 qrs. 9⅔ lbs.	= about 2 tons 15 cwt. 0 qr. 24 lbs.
No. 2.	About 5 cwt. 3 qrs. 18 lbs.	= about 2 tons 15 cwt. 3 qrs. 18 lbs.

In conclusion, I may observe, that the ash of one of the specimens of coal was found to contain very distinct traces of copper. I merely allude to this circumstance, because Mr. Vaux*, in some analyses which he has published of a large number of coals from different localities, mentions copper and lead as occasional constituents—a fact which Mr. Arthur Phillips† has since attempted to refute, on the supposition that the metals discovered by the former gentleman were contained in the water used in the analyses. In the present instance, however, no such error could have been made, because I took the precaution to distil the whole of the water employed in the investigation just before the experiments were commenced, and used glass vessels in all my operations, thus avoiding all chance of metallic impregnation.

Mansion House, Old Park, Bristol,
April 2, 1853.

Researches on the Stannæthyles. *By* Prof. C. Löwig.

[Concluded from page 154.]

In the three preceding numbers, the results of the investigation of these remarkable compounds of tin were given; what follows contains the opinion of the author of the constitution of these bodies.

From these investigations it appears, that, simultaneously with radicals themselves, their iodides are also formed during the action of iodide of æthyle upon an alloy of tin and sodium, although this is not always the case. If iodide of æthyle act upon alloy of antimony and potassium, iodide of stibæthylium ($StAe^4$)I is obtained, together with stibæthyle, $StAe^3$. The formation of the former results simply from the union of 1 atom of iodide of æthyle with the stibæthyle. The relation of the two compounds is the same as that between ammonia and iodide of ammonium. On the other hand, the relations between the stannæthyles and their corresponding iodides are the same as those between the metals and their haloids.

As has been pointed out by Cahours, iodide of stannæthyle, (SnAe)I, is obtained together with iodide of tin, when iodide of æthyle and tin are exposed in a closed tube to a temperature of 356° F. The iodide of tin can only be formed by taking the iodine

* Quarterly Journal of the Chemical Society, vol. i. † *Ibid.*, vol. ii. p. 1.

from the iodide of æthyle; æthyle must be set free, which unites with the tin and stannæthyle. If we now suppose that the stannæthyle reduces another portion of iodide of æthyle, with formation of iodide of stannæthyle, it is evident that æthyle and stannæthyle must be produced. Cahours says nothing of the occurrence of this substance; the author, however, believes that stannæthyle was formed with the iodide of stannæthyle. Cahours extracted the mass, after the reaction had taken place, with alcohol, in which stannæthyle is insoluble; he therefore found in the solution only the iodide, the stannæthyle remaining in the residue. During the action of iodide of æthyle upon tin and sodium, no iodide of tin is formed, and the haloids of stannæthyle are immediately reduced when brought into contact with sodium or potassium. With regard to the simultaneous production of the radicals and their corresponding iodides during the action of iodide of æthyle upon tin and sodium, two explanations may be given, both agreeing in their final results. The simplest case is the formation of stannæthyle, SnAe, and iodide of stannæthyle, (SnAe)I. According to one view, the results of the first reaction are stannæthyle and iodide of sodium, $SnNa+AeI=SnAe+NaI$. The stannæthyle now acts upon a second portion of iodide of æthyle, producing iodide of stannæthyle, whilst the æthyle set free combines with the excess of tin, $SnAe+Sn+AeI=(SnAe)I+SnAe$. But if the sodium be in excess, this alone acts as a reducing agent upon the iodide of æthyle, and in this case no iodide of stannæthyle results. It may also be supposed that an excess of sodium may entirely or partially reduce the iodide of stannæthyle formed. The other explanation is as follows:—In the first moment of action, 2 atoms of iodide of æthyle react upon 2 atoms of tin and 1 atom of sodium, forming stannæthyle, iodide of stannæthyle and iodide of sodium, $2AeI+2Sn+Na=SnAe+(SnAe)I+NaI$. In the second moment, the iodide of stannæthyle formed is reduced, either entirely or partially, by the sodium which is still present. When iodide of æthyle acts upon tin alone, a portion of the latter takes the place of the sodium, and the explanation of the process is consequently the same. When 4 atoms of iodide of æthyle react upon 4 atoms of tin and 3 atoms of sodium, 1 atom of iodide of elaylstannæthyle and 3 atoms of iodide of sodium are formed, $4Sn+3Na+4AeI=(Sn^4\,Ae^4)I+3NaI$; and in the same manner, when 3 atoms of iodide of æthyle act upon 2 atoms of tin and 2 atoms of sodium, 1 atom of iodide of methstannæthyle and 2 atoms of iodide of sodium are obtained, $2Sn+2Na+3AeI=(Sn^2\,Ae^3)I+2NaI$. If sodium be still present, the iodine is extracted from the iodides, and the pure radicals are thus formed; so that 2 atoms of tin, 3 atoms of sodium, and 3 atoms of iodide of æthyle give 1 atom $Sn^2\,Ae^3$ and 3 atoms NaI. Thus the facts, that various compounds may be produced according to the composition of the alloy, according as the iodide of æthyle is or is not in excess, or even according to the force of the action, which may be modified by a greater or less addition of sand, and that, when the operation

is repeated with altered proportions, totally different results are often obtained, may be explained in a very simple manner.

Wurtz was the first to show, that the hydrogen in ammonia may be partially replaced by æthyle; and it appears from the numerous investigations of Hofmann, that the radicals of the methyle and benzide groups in general possess the faculty of replacing the hydrogen in that substance, not only partially, but even entirely, forming compounds agreeing in all their properties with ammonia, even excelling it in their basic properties. As the hydrogen of ammonia may be replaced by the organic radicals, so also may its nitrogen by arsenic, antimony and bismuth; thus the compounds AsH^3, SbH^3, and no doubt also a hydruret of bismuth, BiH^3, represent ammonia, NH^3; and corresponding with these hydro-compounds are stibæthyle, $SbAe^3$, stibmethyle, $SbMe^3$, bismuthæthyle, $BiAe^3$, &c. Like ammonia, the whole of the radicals of this group form with 1 atom H, Me, Ae, &c. metal-like bodies, which approach very closely to the alkaline metals, and furnish compounds endowed with all the characters of inorganic salts.

If the stannæthyles be compared with the above-named radicals, they exhibit different properties in every respect. Whilst stibmethyle, $SbMe^3$, only becomes a metallic body, stibmethylium, by taking up 1 atom of methyle, the stannæthyles themselves behave as metals. Methstannæthyle, $Sn^2 Ae^3$, combines directly with 1 atom of oxygen to form a base, which agrees perfectly in its alkaline properties with the oxide of stibmethylium; and whilst the radicals of arsenic, bismuth, and antimony contain only 1 atom of metal, several atoms of tin are present in the stannæthyles. On the other hand, the latter undoubtedly correspond to well-known organic radicals composed of carbon and hydrogen. Thus if we replace the atoms of æthyle in the stannæthyles by hydrogen, and the atoms of tin by carbon—

Metylenstannæthyle....	$Sn^2 Ae^2$	=	metylene	$C^2 H^2$
Elaylstannæthyle.....	$Sn^4 Ae^4$	=	elayle	$C^4 H^4$
Acetstannæthyle	$Sn^4 Ae^3$	=	acetyle	$C^4 H^3$
Methstannæthyle.....	$Sn^2 Ae^3$	=	methyle	$C^2 H^3$
Æthstannæthyle	$Sn^4 Ae^5$	=	æthyle.....	$C^4 H^5$

So that we come to the result, that as the nitrogen in ammonia and its corresponding compounds with æthyle, methyle, &c. may be replaced by arsenic, antimony and bismuth, the carbon in the organic radicals is replaceable by tin (and also by lead), and also to the further conclusion, that radicals consisting of tin and hydrogen must be obtainable, which will represent the hydrocarbyles in the same manner that ammonia is represented by antimoniuretted and arseniuretted hydrogen. Experiments made with these views have already shown so much, that what has just been said is not simply the result of speculation, but is grounded in truth.

If the atoms of tin combined with the æthyle in the stannæthyles be replaced by atoms of carbon, radicals are produced which agree with the formulæ $C^2 Ae^2$, $C^4 Ae^4$, $C^2 Ae^3$, $C^4 Ae^3$ and $C^4 Ae^5$, and

which stand in the same relation to metylene, C^2H^2, elayle, C^4H^4, acetyle, C^4H^3, methyle, C^2H^3, and æthyle, C^4H^5, as æthylamine, NAe^3, to ammonia, NH^3, or stibæthyle, $SbAe^3$, to antimoniuretted hydrogen, SbH^3. The hydrocarbyles, as is well known, divide, according to the proportions of their carbon and hydrogen, into two classes. Those of the first, which the author calls *hydroisocarbyles*, form an ascending series, of which each succeeding member contains C^2H^2 more than the preceding one; thus methyle$=C^2H^3$ and æthyle$=C^4H^5$, formyle$=C^2H$ and acetyle$=C^4H^3$. The same difference also exists between methstannæthyle$=Sn^2Ae^3$ and æthstannæthyle$=Sn^4Ae^5$, and also between metylenstannæthyle$=Sn^2Ae^2$ and elaylstannæthyle$=Sn^4Ae^4$; and there is perhaps no doubt that radicals may also be attainable agreeing with the formulæ Sn^6Ae^8, &c. The radicals of the second class, the *hydropolycarbyles*, are distinguished from those of the first by an addition of 2, 4, 6, 8 atoms of carbon. In his 'Chemie der organischen Verbindungen,' the author indicated that the hydropolycarbyles are to be regarded as combinations of the hydroisocarbyles with carbon; and this view was more distinctly expressed in his 'Grundrisse der organischen Chemie.' Thus the author supposed that allyle, C^6H^5, is a compound of C^4H^5, or æthyle, with $C^2=C^2$, C^4H^5 or C^2Ae. It is very probable that the volatile oils belonging to the terebene group, which in many respects behave as radicals, have a similar composition. If 2 atoms of carbon be deducted from the empirical formula of citron-oil, $C^{10}H^8$, there remains $C^8H^8=2(C^4H^4)$; and if the sign El be put for C^4H^4, the rational formula of citron-oil is C^2El^2, and that of oil of turpentine C^4El^4, corresponding with metylenstannæthyle, Sn^2Ae^2, and elaylstannæthyle, Sn^4Ae^4. The great number of compounds consisting of equal numbers of atoms of carbon and hydrogen, which are composed of C^6H^6, $C^{10}H^{10}$, may be referred to similar formulæ; thus $C^6H^6=C^2$, $2C^2H^3=C^2Me^2$; $C^{10}H^{10}=C^2$, $2C^4H^5=C^2Ae^2$. If a carburet of sodium could be successfully prepared, radicals would be obtained by the action of iodide of æthyle upon it, which would correspond with stannæthyle. It has long been known, that, during the solution of cast iron in dilute acids, carburetted hydrogens are formed, which consist of several atoms of carbon and hydrogen. So, no doubt, during dry distillation, simple radicals, such as methyle, elayle and acetyle, are first formed; these then combine with carbon to form benzine, toline, naphthaline, creosote, &c., and in the case of nitrogenous substances, with nitrogen to form methylamine, &c. At the commencement of this memoir a radical was mentioned, which consists of Sn^6Ae^4, and which no doubt was formed by the action of iodide of elaylstannæthyle upon the tin and sodium still present:—$Sn^2+Na+(Sn^4Ae^4)I=Sn^6Ae^4+NaI$. The formula of this radical is consequently Sn^2, (Sn^4Ae^4). If the atoms of tin be replaced by carbon, C^2, (C^4Ae^4) is obtained, a formula, in which the atoms of carbon appear in three groups, the total number being 22. If C^4Ae^4 be characterized as elaylcarboæthyle, and represented by the sign X, the formula is C^2X, corresponding with formyle, C^2H.

Thus very complicated relations appear to be referable to very simple expressions, and they find an unforced explanation according to the radical theory, and even according to the radical theory in its original form as it was established by Berzelius. Thus there are but few radicals, primary or simple radicals, which, like the elementary substances, combine with carbon in the same atomic proportions as hydrogen to form new radicals, and which can repeat the same part.

For comparison with the above view, the author now returns to that of Cahours. Cahours regarded stannæthyle as iodide of æthyle in which the iodine is replaced by tin $=C^4\,\frac{H^5}{I}=C^4\,\frac{H^5}{Sn}$, and thought he found the proof of the correctness of his view in the fact, that neither iodine nor tin was to be detected in these compounds by the ordinary reagents. The tin certainly cannot be ascertained in this manner in the stannæthyles; but, on the contrary, if nitrate of silver be added to the alcoholic solution of iodide of æthyle, iodide of silver is immediately precipitated, with formation of nitrate of æthyle; the iodine is also instantaneously separated from iodide of æthyle by chlorine. According to the view of Cahours, methstannæthyle must correspond with a radical $=C^{12}H^{17}$, in which 2 atoms of hydrogen are replaced by 2 atoms of tin $=C^{12}\,\frac{H^{15}}{Sn^2}$, or represent a combination $=2\left(C^4\,\frac{H^5}{Sn}\right)+C^4H^5$.—*Chem. Pharm. Centralblatt*, Dec. 11, 1852, p. 889.

On the Formula for Moritannic Acid.
By Dr. Rudolph Wagner.

Laurent has recently adopted the formula proposed by Strecker for the tannic acid of the oak-gall; and upon the assumption that all the varieties of tannic acid have analogous compositions, has further altered the formulæ of all those which have been analysed. Thus he assigns to the moritannic acid discovered by the author the formula $C^{44}H^{22}O^{26}$. He likewise states, that with one exception (melted catechuic acid), all the formulæ proposed by him agree with the analytical data as well as, or better than, those previously adopted. In its special reference to moritannic acid, the author considers that Laurent's view is incorrect, for the analytical data obtained by him are—

	I.	II.	III.	IV.	V.
Carbon	55·55	55·16	55·18	54·94	55·00
Hydrogen ..	4·53	4·58	4·50	4·26	4·19
Oxygen					

And these lead to the formula $C^{18}H^8O^{10}$. These two formulæ require respectively—

	Wagner.		Laurent.	
Carbon.....	18	55·102	44	53·44
Hydrogen.....	8	4·081	22	4·45
Oxygen	10	40·817	26	42·11

In a theoretical point of view, the objection may be urged against the adoption for tannic acids of formulæ with 40 C and 44 C, that it follows from the analyses of tannates that 18 C require 3 equivs. RO for saturation. But the formulæ of Strecker and Laurent would represent acids requiring at least 6 equivs. of base to form neutral salts, that is sexi- or octobasic acids. The author considers that there are no facts which prove the existence of sugar in moritannic acid, or justify its classification among the glucosamides. But even supposing the presence of sugar to have been proved, it would still be more correct to infer that moritannic acid is a conjugate substance, one of whose components is convertible into grape-sugar by the action of dilute sulphuric acid. The opinion that tannic acid is a conjugate of gallic acid with a hydrate of carbon is not novel, but was put forward in 1847 by Mulder, who regarded tannic acid as a conjugate of gallic acid with gum.—*Journ. für Prakt. Chem.*, 1853.

On the Use of Fatty Acids as a Source of Light.
By J. Cambacérès.

The author has endeavoured to reduce the cost of fabrication of these fatty acids by employing such materials as will furnish a by-product more valuable than the sulphate of lime obtained by the saponification with lime. He has succeeded in preparing in this way sulphate of alumina, a substance largely used in dyeing.

For this purpose, he first saponifies the fat with potash or soda lye. The soap, containing an excess of alkali, acts upon clay so as to dissolve the alumina, which combines with the fatty acids, forming a soap which is insoluble in the alkaline liquid, and the alkali is again set free. The alumina-soap may be separated as a gelatinous precipitate by an excess of alkali, by a large quantity of water, or by saline solutions. The gelatinous character of the alumina soap facilitates its decomposition by acids, and the alumina salt may be obtained by evaporation, during which the silica likewise taken up by the alkali is separated.

The decomposition of soap by alumina is undoubtedly owing to the affinity of alumina for fat acids and the insolubility of the alumina soap in alkaline lye.

In order to prepare the fat acids in this way at the least possible cost, care must be taken that in washing the soap as little alkali as possible be left. However, a residue of alkali is not objectionable on any other grounds, for when the soap is decomposed with sulphuric acid, it forms alum. It follows therefore from these facts, that in places where clay free from iron can be procured, the fabrication of acetate and sulphate of alumina may very advantageously be combined with that of stearic acid, because, according to the author, the relative cost of production, notwithstanding the high price of alkalies, is less than when lime is employed in the saponification.—*Comptes Rendus*, vol. lvii. p. 441.

ANALYTICAL CHEMISTRY.

New Processes for determining Copper, Lead and Sulphuric Acid, by the Method of Volumes. *By* Dr. H. SCHWARTZ.

I. *Determination of Copper.*

WHEN a solution of a copper salt is mixed with a large quantity of tartaric acid and potash, a deep blue-coloured liquid is produced. When this is warmed, and a sufficient quantity of a deoxidizing substance, such as arsenious acid or grape-sugar, is added, the whole of the copper is precipitated after a short time as suboxide.

Pelouze has already attempted to take advantage of this reaction, by adding to an alkaline solution of oxide of copper a solution of grape-sugar of known per-centage until the deoxidation was complete. However, this method proved inapplicable, from the fact that the quantity of grape-sugar necessary to produce perfect deoxidation is not constant, but dependent upon the temperature, alkalinity of the liquid, and various conditions, the presence of which it would be difficult to ensure*.

The author therefore proposes to effect the quantitative determination of copper by means of the reaction which takes place between perchloride of iron, hydrochloric acid and suboxide of copper—

$$Cu^2O + Fe^2Cl^3 + HCl = 2CuCl + 2FeCl + HO;$$

and to determine by means of permanganate of potash the quantity of subchloride formed, from which that of the copper in the substance analysed may be calculated.

This method is capable of giving results not less exact than Marguerite's process for the determination of iron, with which indeed it is identical; and it has the further advantage of not being subject to the probable error resulting from the imperfect washing of the suboxide of copper in the direct determination.

The process is carried out in the following manner:—The weighed copper compound is dissolved in either water or hydrochloric acid, the solution introduced into a capacious porcelain or platinum dish, and mixed in the cold with a solution of neutral tartrate of potash and caustic potash. The clear blue liquid thus obtained is then mixed with an aqueous solution of grape- or milk-sugar in sufficient quantity, and the whole warmed upon a water-bath until the clear liquid begins to show a brownish colour at the edges, a sign that all the copper is precipitated, and that the potash is acting upon the sugar. The grape-sugar used may be either ordinary starch-sugar or a solution of honey; but it is perhaps best to use pure milk-sugar. When the precipitate has settled, which takes place very rapidly, the liquid is filtered through ordinary bibulous paper. The deep brown-coloured liquid which passes through is almost opake, and at the surface of contact with the wash-water there sometimes appears to be a yellowish turbidity, which however is not owing to the presence of suboxide of copper, and disappears on mixing the

* Mulder's method for determining grape-sugar, by weighing the suboxide of copper precipitated, cannot therefore be absolutely accurate, independently of the fact that this oxide is very difficult to wash.

liquids. The precipitate must be washed with hot water until the filtrate is colourless. Sometimes, and especially when the mixture has been heated too much, the suboxide of copper appears rather coloured. However, this is merely owing to its being in a rather denser state, and has no influence upon the analytical result.

It frequently happens that a small portion of the suboxide of copper adheres firmly to the sides of the basin; but as the precipitate is afterwards dissolved in the same basin, this circumstance is of no consequence. When the precipitated suboxide is perfectly washed, it is returned into the basin, and mixed with an excess of perchloride of iron and dilute hydrochloric acid. The perchloride of iron must, of course, be free from protochloride and nitric acid, but may contain a considerable excess of hydrochloric acid. It is therefore advisable to evaporate the perchloride of iron to dryness with a little nitric acid and an excess of hydrochloric acid, so as to ensure its being in a proper state.

On gently warming the mixture of suboxide of copper and perchloride of iron, the subchloride of copper formed dissolves readily, especially when the surface is renewed by stirring. The green liquor is then filtered into a capacious flask, and the filter, together with the remains of the previous one, thoroughly washed with hot water. The filtrate is mixed with a little hydrochloric acid, and cold water added until the temperature is about 96° F., so as to prevent the disengagement of chlorine on the addition of the permanganate of potash. The quantity of protochloride of iron present in the liquid is then determined by means of a solution of permanganate of potash of known strength, and the quantity of copper calculated from the result thus obtained, every equivalent of iron representing an equivalent of copper. The author estimates the value of the solution of permanganate by means of iron wire. He takes 0·281 grm. of the best piano-string wire, but on account of the impurities it contains, calculates it as 0·280 grm., or 1 equiv. of iron (H=0·01). The solution of permanganate is made of such strength that this quantity of iron is oxidized, or, as in the present case, converted into perchloride by 20 cub. centims. of it. A more dilute solution gives still more accurate results.

When other metals are present in the substance analysed, they may either be separated before the precipitation of the suboxide of copper, or remain dissolved after that has been effected, and are then removed by mere filtration. Gold and platinum do not dissolve in nitric acid; silver and suboxide of mercury may be separated by hydrochloric acid, or equally well with oxide of mercury by potash, even in the presence of tartaric acid. Antimony and tin remain, after the treatment with nitric acid, as oxides. Oxides of lead and zinc, as well as alumina and oxide of chromium, dissolve in the potash, and oxides of bismuth and manganese, when tartaric acid is present.

Oxide of nickel is indeed partially precipitated; but as it has no deoxidizing action, this has no influence upon the result.

When a solution of perchloride of iron is mixed with a sufficient

quantity of tartaric acid and potash, a brownish solution is obtained, which deposits peroxide of iron after long boiling, but not on heating it in a water-bath. Even if the suboxide of copper should be mixed with a small quantity of this peroxide of iron, it merely gives rise to the formation of a little more perchloride of iron on treating the precipitate with perchloride of iron and hydrochloric acid, without in any way influencing the determination of the copper; while in Pelouze's process the precipitation of the peroxide of iron by ammonia is always attended by a slight loss of copper, as oxide of copper is carried down with the peroxide of iron.

Analyses of sulphate of iron, bronze turnings, brass, German silver coins, copper mat, &c., by this process furnished perfectly satisfactory results. The following results will testify to the accuracy of the process:—

1. 0·280 grm. iron (1 equiv.) required 17·5 cub. cent. permanganate.
2. 0·317 grm. voltaic copper (1 eq.) req. 17·5 cub. cent. permanganate.
   0·280 grm. of iron required..... 17·1 cub. cent.
   0·317 grm. voltaic copper required 17·1 cub. cent.

This analytical method appears to be especially suited to the requirements of copper-smelters; it likewise admits of analyses being made while the metal for bronze castings is in a state of fusion, so that, according to the results obtained, any necessary addition of copper or tin may be made.

II. *Determination of Lead.*

In order to avoid the inconveniences and want of accuracy of the several modes of determining lead by the method of volumes, either by adding a solution of sulphuret of sodium to the clear solution of nitrate of lead in excess of potash until there is no longer any precipitation of sulphuret, or when zinc is present, until white sulphuret of zinc begins to be thrown down, or by treating the boiling alkaline solution of lead with permanganate of potash until it acquires a green colour,—the author proposes a method based upon the characters of the chromate of lead.

On adding to a solution of oxide of lead in nitric or acetic acid with a moderate excess of acid, an excess of a solution of bichromate of potash, the lead is entirely precipitated as neutral chromate, which on the application of a gentle heat deposits very rapidly, and may be readily filtered and washed. The presence even of a small quantity of hydrochloric acid is no hindrance, and it is only when this acid is present in large excess, that there is a necessity to add an excess of acetic acid after the addition of the bichromate solution. Even sulphate of lead, at least when freshly precipitated, is completely converted into chromate when digested with the bichromate of potash. The use of an excess of bichromate of potash to effect the perfect precipitation of acid solutions is necessary, because then the acid combines with a part of the potash; so that a chromate of potash, containing several equivalents of acid, is left, and this has no solvent action upon the chromate of lead.

It is most convenient to precipitate the chromate of lead in a

porcelain dish, after having previously warmed the liquid in a water-bath. The precipitate is then separated by filtration, well washed, and then returned into the dish, where it is treated with an excess of an acid solution of protochloride of iron of known value, and the whole gently warmed. The chromate of lead dissolves completely—

$$2(PbO, CrO^3)+6(FeCl)+8HCl=2PbCl+Cr^2Cl^3+3(Fe^2Cl^3)+8HO.$$

If now the quantity of protochloride of iron which remains is determined by means of permanganate of potash, and deducted from the original quantity of iron used in the form of protochloride, the difference gives the quantity which has been converted into perchloride by the chromic acid, and indicates at the same time the quantity both of lead and chromic acid present. According to the above equation, the lead bears such a proportion to the iron, that every 3 equivs. of iron converted into chloride correspond to 1 equiv. of lead.

To effect this decomposition, the dark green liquid is rapidly filtered into a flask, the filter washed with hot water, and the permanganate solution then added. Notwithstanding the dark green colour of the liquid, the reddening produced by the permanganate is very distinctly perceptible; however, as a minute excess is in all cases necessary, it is advisable not to take into account the last few drops added (=0·1 cub. cent.).

The only metal whose presence offers any serious obstacle to the accurate determination of lead by this method is bismuth. It is stated in analytical manuals, that chromate of bismuth is soluble in nitric acid, and is thus distinguishable from chromate of lead. However, this must only be understood *cum grano salis*. It is true that the freshly-precipitated bismuth salt is dissolved by strong nitric acid, and at the same time converted into an acid chromate. But this strong acid likewise dissolves a small quantity of chromate of lead. On the addition of water, and still more on the addition of the necessary excess of chromate of potash, basic chromate of bismuth is again precipitated, and mixes with the chromate of lead.

The author attempted to precipitate the oxide of bismuth by means of potash, but it appeared that some oxide of lead was likewise carried down. By mixing the nitric acid solution of the two metals with acetate of soda and heating, he succeeded in separating the greater part of the oxide of bismuth, although there still remained 3 or 4 per cent. mixed with the chromate of lead.

Oxide of silver and suboxide of mercury, both of which form chromates which are insoluble in weak nitric acid, may be separated by very dilute hydrochloric acid without causing any loss of lead. The suboxide of mercury may likewise, by boiling with nitric acid, be converted into protoxide, which is not precipitated by chromic acid. All the other chromates are soluble in water or in acids.

III. *Determination of Sulphuric Acid.*

For this purpose the author employs three solutions:—

1. A normal solution of bichromate of potash (equiv. 147·8), con-

taining 4·926 grm. KO $2CrO^3$ in the litre; 0·2463 grm.=$\frac{1}{6}$ equiv. in 50 cub. cent.

2. A normal lead solution, containing 11·056 grm. PbO NO^5 (equiv. 166) in the litre; 0·5533 grm.=$\frac{1}{3}$ equiv. in 50 cub. cent.

These solutions are of such a strength, that when equal volumes of each are mixed, the oxide of lead and chromic acid are completely precipitated as neutral chromate of lead.

3. A normal protochloride of iron solution, containing 5·600 Fe in the litre; 0·280 grm. Fe=1 equiv. in 50 cub. cent.

The following is the mode in which the process is carried out. The sulphate, which must contain less than 0·1333 grm. SO^3, is dissolved in water slightly acidulated with nitric acid, and then mixed with 50 cub. cent. of the lead solution. The filtrate separated from the precipitated sulphate of lead is gently warmed, and mixed with 50 cub. cent. of the solution of bichromate of potash, and the precipitated chromate of lead filtered and washed. As a part of the oxide of lead is precipitated in the first instance by the sulphuric acid, the whole of the chromic acid is not precipitated on the addition of the bichromate of potash, but a portion remains which is larger in proportion to the quantity of sulphuric acid present in the substance analysed; and the ratio of these substances is such, that 1 equiv. of chromic acid remaining unprecipitated represents 1 equiv. of sulphuric acid. The liquid filtered from the chromate of lead is then to be mixed with 50 cub. cent. of the iron solution containing free hydrochloric acid, and the whole slightly warmed, so as to obviate the reduction of the chromic acid to $Cr^2O^3+CrO^3$.

The green liquid thus obtained is then treated with a solution of permanganate of potash, in order to determine the quantity of protochloride of iron present. The calculation of the result from the data thus obtained is very simple. If, for instance, the solution of permanganate was of such a strength that 50 cub. cent. of the iron solution requires 17·3 cub. cent. to convert it into perchloride, then the iron solution will require less than 17·3 cub. cent. after it has been mixed with the liquid containing chromic acid. If then the necessary quantity of permanganate=a cub. cent., then $17{\cdot}3-a$ represents the quantity of chromic acid remaining in the liquid; and as this is also equivalent to the sulphuric acid, the following proportion gives the quantity of sulphuric acid=x:—

$$17{\cdot}3 : 17{\cdot}3-a=0{\cdot}1333 : x.$$

The presence of free hydrochloric acid in the iron solution does not precipitate chloride of lead, because the solution of lead is too weak. Phosphoric, nitric, or acetic acids do not influence the results. Among the bases, those only can be prejudicial which give with chromic acid precipitates insoluble in nitric acid. However, oxides of silver and bismuth and suboxide of mercury may be previously separated by potash. The deoxidizing bases, such as protoxide of tin or iron, must likewise be peroxidized beforehand.—*Ann. der Chem. und Pharm.*, vol. lxxxiv. p. 84.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Preparation of Molybdic Acid from the native Molybdate of Lead. *By* C. ELBERS.

As the native molybdate of lead has lately been found in rather large quantities in Bavaria, it is of importance to have some simple and cheap process for obtaining molybdic acid from it. By such a process, the use of molybdic acid or its compounds in the arts will be facilitated; of which Keller* has already raised expectations, by proposing to employ the yellow compound of molybdic acid with phosphoric acid and ammonia in dyeing, calling it mineral indigo on account of the blue colour produced by means of it. For analytical purposes, moreover, the cheap and easy preparation of molybdic acid will be of use, as by this means the molybdate of ammonia, which, as has been shown by Svanberg and Struve, is the most sensitive test for phosphoric acid, will become more available for the qualitative determination of that acid. I was therefore requested by Professor Liebig to make experiments on the preparation of molybdic acid; these I performed in his laboratory, and communicate their result in the present memoir.

Until recently, only one method, proposed by Wittstein, was known to us for the preparation of molybdic acid from the native molybdate of lead: this consisted in transforming the molybdic acid into sulphuret of molybdenum by fusion with liver of sulphur, and extracting the molybdic acid from this by roasting and oxidation with nitromuriatic acid. This method however is somewhat circuitous, and not fitted for the preparation of large quantities of molybdic acid.

Delffs therefore recently proposed another method†, in which he treated the molybdate of lead with dilute nitric acid, to remove the carbonic acid salts contained in it, and then boiled the residue with concentrated nitric acid, evaporated this, and repeated this operation twice; the nitrate of lead formed is then extracted with water, and the free molybdic acid, which is left behind, dissolved in ammonia. Delffs states also, that, after careful treatment with nitric acid, a larger or smaller quantity of undecomposed ore remains behind, from which it follows that the decomposition is imperfect. Whether this undecomposed residue be so small in quantity that the method

* Dingler's Polytechn. Journ., cxxi. p. 465.

† Poggendorff's Annalen, lxxxv. p. 450.

loses nothing thereby, can only be decided by the amount obtained by perfect operations. As Delffs communicates nothing on this subject, I endeavoured to perform its quantitative determination, by evaporating the solution of molybdate of ammonia obtained by this method, weighing the quantity, reducing a portion of it to the state of oxide by exposure to a current of hydrogen gas in a platinum crucible at a red heat, and from this calculating the quantity of molybdic acid.

I procured the native molybdate, which I employed in my investigations, from J. P. Biebel, of Gannisch; the principal foreign matters contained in it were carbonate of zinc and oxide of iron.

Although the first operation of Delffs' method, namely the extraction of the carbonates by diluted nitric acid, appears superfluous to me, as those salts are also decomposed by direct treatment with concentrated nitric acid, and got rid of by the solution of the nitrate of lead, I have nevertheless in this determination taken care to follow Delffs' directions exactly, in order to obtain a corresponding result.

For this purpose I treated ½ a pound of native molybdate of lead, after the preliminary extraction of the carbonates by means of diluted nitric acid, with 1½ lb. of concentrated nitric acid, which I added in three portions one after another, evaporating almost to dryness between each addition. This operation, which required about six hours for its completion, was performed in a porcelain dish on the sand-bath. After the last portion of the nitric acid was evaporated, the mass was treated with water, and washed on a filter until the filtrate no longer gave a precipitate with sulphuric acid; the washing-water became at last somewhat turbid on passing through the filter, which may be avoided by the addition of a little nitric acid to it. The residue, which resembled the undecomposed ore in its yellow colour, was extracted by ammonia, in which process a considerable quantity remained undissolved. The ammoniacal solution, analysed in the manner described above, contained 24·22 grms. MoO^3, which corresponds with 9·7 per cent. MoO^3 out of the native molybdate of lead.

The residue was then again similarly treated with 1 lb. of nitric acid; and in order to allow the nitric acid a longer time for its action, about nine hours were thus employed; it was then washed with water, and dissolved in ammonia. I thus obtained 32·77 grms. MoO^3=13·1 per cent. from the ore.

Although the residue of this operation no longer appeared yellow, but perfectly white, it still contained molybdate of lead; perhaps an acid molybdate of lead had been formed. It was therefore again subjected to the same treatment with ½ a pound of nitric acid, by which 7·01 grms. MoO^3 were produced=2·8 per cent. on the ore.

The residue, which was no longer considerable, was no further operated upon, although still containing molybdate of lead. From this result it follows that the ore can be completely decomposed by frequent treatment with nitric acid, but not in one operation. An expenditure of 3 lbs. of nitric acid upon ½ a pound of the ore pro-

duced from it thus 25·6 per cent. of molybdic acid. This method otherwise so simple, is unfortunately protracted in consequence of the imperfect decomposability of the ore by nitric acid.

If equal parts of powdered ore and calcined soda, previously intimately mixed, be melted together in a Hessian crucible until the whole is fluid, and then poured out, a hard yellowish mass is obtained. This, when powdered and boiled in water, gives a solution of molybdate of soda, which is contaminated with some oxide of lead and phosphate of soda, the ore containing phosphoric acid. The oxide of lead may be removed by adding some carbonate of ammonia to the solution, allowing it to stand in a warm place for some time and filtering, when, by evaporating the solution to dryness with the addition of some muriate of ammonia, and dissolving in water, a beautifully white molybdic acid salt, which is difficult of solution, is obtained; it is, however, contaminated with phosphoric acid. On washing, some molybdic acid is dissolved, so that loss cannot be entirely avoided.

If the mass evaporated with muriate of ammonia be heated to redness in a Hessian crucible, oxide of molybdenum is obtained; and, after the muriate of soda has been got rid of by boiling and washing in water, to which at last some nitric acid is to be added, molybdic acid is readily procured by heating with concentrated nitric acid and evaporating to dryness. The red heat must not be continued too long, nor must the access of the air be permitted during this operation, as otherwise considerable quantities of oxide of molybdenum may be changed by oxidation into acid, which is volatile.

If the solution formed from the mixture of ore with carbonate of soda be boiled to concentration with an excess of nitric acid, molybdic acid is thrown down as a white precipitate. This method has been already given by Christl, and as it is perhaps the best way to prepare molybdic acid from molybdate of soda, I subjoin the result of this operation. I must however observe, in the first place, that disadvantages attend the use of both a Hessian and an iron crucible for the fusion with carbonate of soda; the first being readily fused by the alkali, and the second attacked by the oxide of lead produced. To avoid the latter as much as possible, I took—

$\frac{1}{2}$ lb. of native molybdate of lead,
$\frac{1}{2}$ lb. of calcined soda, and
$2\frac{1}{2}$ oz. of iron filings,

intimately mixed, fused them together, and as soon as the mass became fluid poured it out. The lead had separated partly as regulus, partly on the iron filings, and a part remained still in the fused mass in the form of oxide. This was pulverized, boiled, and washed with water; the filtrate evaporated after the addition of 1 lb. of nitric acid until the disappearance of this acid, then diluted with water and filtered. The well-washed residue was a beautifully white mass, which was free from phosphoric acid; it was dried, and then furnished—

48·9 grms. MoO^3=19·5 per cent. MoO^3 from the ore.

This molybdic acid was free from phosphoric acid; it was not, however, quite pure; it did not dissolve completely in ammonia, and was not perfectly volatile when heated to redness on platinum foil; the latter no doubt arises from its containing some soda. I consider it therefore as molybdic acid, which still retains some impurities in consequence of imperfect washing. As the portion of the filtrate which first passes through contained a considerable quantity of molybdic acid, this was evaporated nearly to dryness, by which the excess of nitric acid was nearly all driven off; it was then dissolved in water, filtered and well washed. After drying I obtained—

14·8 grms. MoO^3=5·9 per cent. MoO^3 from the ore.

This was of a pale citron-yellow colour, and left, when dissolved in ammonia, a considerable residue, in spite of long washing; like the above, it was not perfectly volatile on platinum foil; it contained a little phosphoric acid. The filtrate in this case also contains at first some molybdic acid, which however is not to be extricated in this manner.

The decomposition of the ore, produced by fusion with carbonate of soda, is tolerably complete, for the residue of the washing exhibits no very distinct reaction of molybdic acid.

I have tried fusing the ore with carbonized tartar instead of carbonate of soda. Thus I fused—

½ lb. of native molybdate of lead with
½ lb. of carbonized tartar,

until no more gas escaped; by this all the lead was reduced, and collected as regulus in the bottom of the crucible. The black fused mass was taken out, dissolved in water, and treated like that obtained with carbonate of soda; for supersaturation I added ¾ lb. of nitric acid, when the solution was concentrated; it was then evaporated a little, and the molybdic acid was precipitated very rapidly. By this means I obtained—

45·5 grms. MoO^3=18·2 per cent. MoO^3 from the ore.

It was of a dazzling white colour, and free from phosphoric acid; it dissolved completely in ammonia, but left a slight residue when heated on platinum foil. The filtrate still contained much molybdic acid; it was therefore evaporated to dryness, to remove the excess of nitric acid, then dissolved in water and filtered. The residue was at first pale citron-yellow, but became perfectly white after long washing; it gave only—

1·5 grm. MoO^3=0·6 per cent. MoO^3 from the ore.

The filtrate still contained molybdic acid, which however was neglected.

The fusion with soda appears from this to give a more profitable result than that with carbonized tartar. It must indeed be remembered, that the molybdic acid obtained by the former method was

not so pure, and that the impurities naturally increased the weight; the loss also by adhesion to the crucible, which it is impossible to avoid in a single experiment, might have been greater in the latter case than in the other. The residue of the melting with tartar and washing with water contains only a trace of molybdenum, and indeed much less than in the treatment with carbonate of soda; the former must therefore give a more favourable result. According to this no molybdic acid is reduced by the carbon, or else the oxide of molybdenum formed must have evaporated through some access of air; this however is not to be supposed, as carbon was still present in excess, and moreover the volatilization could not have taken place completely in consequence of the slight access of air.

Fusion with carbonized tartar has the advantage, that the crucible is not attacked by it, and the lead is completely separated in a metallic form; and I should have tried it again had not the following method appeared to me to merit the preference over all the others for its simplicity, cheapness and good return.

I digest in a porcelain dish on the sand-bath with a good heat—

1 lb. of very finely-powdered molybdate of lead with
1¼ lb. of concentrated English sulphuric acid,

until at last a little sulphuric acid evaporates. The mixture is stirred during this process with a spatula. It is to be continued until a little, taken out upon a glass rod and mixed with water, shows a perfectly white residue, containing no yellow granules of undecomposed ore; this is generally the case in an hour and a half. The resulting blue paste is mixed with much water, by which the sulphate of lead dissolved in the concentrated sulphuric acid is precipitated; the whole is then put into a beaker and washed by decantation, which is readily effected in consequence of the rapid settlement of the sulphate of lead. The decanted fluid is filtered, and lastly the whole brought upon the filter, and again washed until the filtrate is colourless. In this manner a blue solution of molybdic acid in sulphuric acid is obtained, and the residue, consisting of sulphate of lead, is free from molybdic acid; the decomposition is therefore complete. The solution is put into an evaporating dish, about 3 oz. of nitric acid added to it (when the blue colour disappears), and evaporated upon the open fire until the nitric acid begins to be driven off. In this operation the molybdic acid is separated in the form of a voluminous white precipitate; the fluid must therefore be constantly stirred with a spatula, to prevent the settlement of this precipitate and the consequent bubbling. It is then diluted with water, filtered and well washed, until the filtrate neither gives a precipitate with carbonate of soda nor shows the presence of sulphuric acid; lastly, the washing is to be done with water containing nitric acid until the filtrate is not turbid. After strongly drying the precipitate, I obtained—

87·1 grms. MoO^3=17·4 per cent. MoO^3 from the ore.

The filtrate is collected as long as it retains a yellowish colour, and

again evaporated until sulphuric acid is driven off. There was separated thus—

34·2 grms. MoO^3=6·8 per cent. from the ore.

The filtrate was again evaporated to the concentration of the sulphuric acid, by which some molybdic acid was again separated. But in order at once to obtain the last remainder of the molybdic acid, I put the whole into an evaporating dish, and drove off the sulphuric acid completely. The cake thus obtained, boiled in water until it was all finely divided, and evaporated with the addition of some nitric acid, gave—

24·8 grms. MoO^3=4·9 per cent. from the ore.

The filtrate still contained some molybdic acid, but in no considerable quantity; and this loss, the only one occurring by this process, was undeserving of notice.

In order to facilitate the washing of the separated molybdic acid, I extracted the carbonates first of all with dilute nitric acid (1 part of concentrated nitric acid to 6 parts of water), by which only traces of molybdic acid are dissolved, and then treated it as above with concentrated sulphuric acid. In this case care must be taken that no paper from the filter remains attached to the ore, as the residue of sulphate of lead then remains blue, probably in consequence of a reduction of the molybdic acid. By the first evaporation of this sulphuric solution, I obtained from 1 lb. of the ore—

95·8 grms. MoO^3=19·1 per cent. from the ore.

The filtrate was then evaporated to dryness, and furnished—

38·5 grms. MoO^3=7·7 per cent. from the ore.

This treatment with nitric acid is however quite superfluous, and only increases the operations.

The only disadvantage possessed by this method is the evaporation of the sulphuric acid; this may however be omitted, and still a result will always be obtained exceeding that of any of the preceding methods, particularly considering that by the last evaporation to the concentration of the sulphuric acid, even a portion of the last residue of the molybdic acid is extricated. It would be possible, moreover, so as not to lose the molybdic acid remaining dissolved in the sulphuric acid, to employ this sulphuric acid again for the decomposition of the native molybdate of lead; in this case, however, the carbonates must previously be extracted by dilute nitric acid, so as not to have too much sulphate of zinc in solution.

The molybdic acid obtained by this process is, when dried, white with a yellow tinge (that procured by the driving off the sulphuric acid is somewhat greenish), feels like talc, and is free from phosphoric acid. In order to have a convincing proof that it was pure molybdic acid, I reduced a portion of it in a current of hydrogen to oxide of molybdenum; and the results of various experiments agreed within $\frac{1}{4}$ or $\frac{1}{2}$ a per cent. with the quantity of molybdic acid employed.

The bulky precipitate obtained by the evaporation of the sul-

phuric acid solution would appear to be a hydrate of molybdic acid, if there be such a thing, for when the solution was evaporated to dryness, and the residue boiled with a little water with the addition of some nitric acid, the whole swelled into a voluminous jelly, exactly as though the water combined with it.

Although I did not determine the quantity of acid contained in the native molybdate of lead, it appears by what follows that the loss by this method can only be very small. Thus I obtained altogether 29·1 per cent. of molybdic acid from the ore; this represents—

75·5 per cent. of molybdate of lead; by the extraction of the carbonates by means of nitric acid (by which however all the impurities are not removed, a considerable quantity of iron still remaining in the residue), the ore lost—

16·6 per cent.; there is therefore wanting—

7·9 per cent., which consists of oxide of iron, and perhaps also some quartz and lost molybdate of lead.

Svanberg and Struve, in their memoir on molybdenum*, state that phosphoric acid has so great a propensity to accompany molybdic acid in all its combinations, that they could give no other way for the preparation of pure molybdic acid, but the formation of an artificial sulphuret of molybdenum in the dry or humid way. It is therefore of particular consequence that the molybdic acid obtained as above is free from phosphoric acid; I have, however, in several experiments with a solution of molybdate of ammonia contaminated with phosphoric acid, always obtained by crystallization a molybdate of ammonia free from phosphoric acid. Thus, whilst the solution containing phosphoric acid acquired a yellow colour by boiling with the addition of nitric acid, and deposited a yellow precipitate on standing, the crystals obtained from this solution did not exhibit this reaction, *i. e.* their solution remained perfectly colourless on the addition of nitric acid.

Resumé of the Results.

By Delff's method I obtained 9·7 per cent. MoO^3.

By fusion with soda, 25·4 per cent. MoO^3, which however was not quite pure.

By fusion with tartar, 18·8 per cent. MoO^3, only rendered impure by a little potash.

By treatment with sulphuric acid, 29·1 per cent. MoO^3, as pure molybdic acid.—*Ann. der Chem. und Pharm.*, lxxxiii. p. 215.

Chemistry of the Plants of the Family Ericineæ.
By F. Rochleder.

All the plants of this family which have been investigated contain a tannic acid:—

* Erdmann's Journ. für Prakt. Chem., xliv. p. 264–300.

Arctostaphylos uva ursi, gallic acid ..... $=C^{14}H^{6}O^{10}$ in its monobasic lead salt.
Calluna vulgaris, callutannic acid ..... $=C^{14}H^{6}O^{8}$ in salts dried at 212° F.
Rhododendron ferrugineum, rhodotannic acid .... $=C^{14}H^{6}O^{7}$ in salts dried at 212° F.
Ledum palustre, leditannic acid ..... $=C^{14}H^{6}O^{6}$ in salts dried at 212° F.

Erica herbacea contains an exactly similar acid, which, according to preliminary experiments, has the formula $C^{14}H^{8}O^{7}$, and therefore is isomeric with caffeotannic acid and the tannic acid of the *Portlandia grandiflora* (China nova Xauxa), which the author calls eritannic acid. All these acids, with the exception of the gallic acid, strike a green colour with salts of the peroxide of iron. When combined with alkalies, they become rapidly oxidized, and furnish dark solutions. With sulphuric or muriatic acid they all furnish a yellow or red colouring matter, with loss of water or of its elements in the form of water. Gallic acid gives para-ellagic acid; callutannic acid, calluxanthine; rhodotannic acid, rhodoxanthine; leditannic acid, ledixanthine; and eritannic acid, erixanthine.

Callutannic, rhodotannic and leditannic acids, as well as eritannic acid, give yellow precipitates with solution of chloride of tin; the basic lead salts of the above-mentioned acids are yellow, like chromate of lead. With the exception of gallic acid, they all communicate to stuffs prepared with a mordant of a salt of tin, a fine, lasting yellow colour; the same is the case with stuffs prepared with an alum mordant, if chloride of tin and muriatic acid be added.

The Rubiaceæ contain a series of tannic acids, $C^{14}H^{8}O^{n}$, while in the Ericineæ we have a series of tannic acids, $C^{14}H^{6}O^{n}$. The carbon they contain does not, however, as is the case in the tannic acids of the Rubiaceæ, exist in them in two different states, divided between two groups; and they only lose water or its elements when treated with acids, whilst the acids of the Rubiaceæ undergo a splitting under these circumstances.

Besides these acids, all the above-mentioned plants contain a neutral substance, ericoline, which, when warmed with acids in its watery solution, furnishes an essential oil amongst other products. The largest quantity of this substance is contained in *Ledum palustre*; *Arctostaphylos uva ursi* stands next in this respect; *Calluna vulgaris*, *Erica herbacea*, and *Rhododendron ferrugineum* contain very little of it.

Ready-formed essential oil is contained in all the above plants. *Calluna vulgaris*, *Erica herbacea*, and *Arctostaphylos* contain only traces of it; *Ledum palustre* contains the largest quantity; *Rhododendron ferrugineum* a little less.

The leaves of all these plants contain a small quantity of fatty matter, chlorophylle, and a considerable quantity of wax.

Calluna vulgaris, *Erica herbacea*, and *Ledum palustre* contain substances belonging to the pectine series; none of these were found in *Rhododendron* and *Arctostaphylos*.

Citric acid is found in *Ledum palustre*, and in all probability this acid is also present in the other plants in very small quantity.

We have in the family of the Rubiaceæ a series of bodies (*tannic acids*) with 14 equivs. of carbon, accompanied almost throughout by substances with 12 equivs. of carbon (citric and kinovic acids), and less prominently a third series, the members of which (alizarine, quinine, cinchonine) contain 20 equivs. carbon.

In the family Ericineæ, we also find a series (tannic acids) with 14 equivs., and a second with 20 equivs. of carbon.

The essential oils of the *Ledum palustre* and *Rhododendron ferrugineum* contain C^{20}; and the ericinole, which results from ericoline, also contains C^{20}. The arbutine of the *Arctostaphylos uva ursi* is the saccharine compound of arctuvine, which also contains 20 equivs. of carbon (arctuvine$=C^{20}H^{10}O^{7}$). If we suppose 5 equivs. of oxygen in the arctuvine to be replaced by 5 equivs. of hydrogen, we obtain $C^{20}H^{15}O^{2}$, the composition of the oil prepared by Willigk from *Ledum* by means of sulphuric acid.—*Sitzungsb. der Akad. der Wiss. zu Wien*, July 1852.

Report on a Memoir relative to the Action of Water upon various Bodies at a high Temperature and under strong Pressure. *By* A. Reynoso. (MM. Dumas *and* Pelouze, *Reporters.*)

Geology has too often reason to take into consideration the results of the action of water upon substances imbedded at great depths in the earth, to render it necessary here to dwell upon the interest of all investigations of this nature.

M. Alvaro Reynoso places the substances which he desires to study in glass tubes, which are themselves enclosed in gun-barrels.

This little apparatus is plunged into an oil-bath, which is heated to 536° or 572° F., taking the usual precautions against explosion.

Water plays the part of a base in so many cases, that one cannot feel astonished, if, in the experiments that now occupy our attention, in which by the closure of the vessels it becomes actually fixed, it should constitute an energetic base. Thus, for example, M. Reynoso has proved that quinine, which is converted into quinoline by potash under the ordinary pressure, undergoes precisely the same change by the mere action of water at about 482° F.

Phosphoric acid possesses the property of forming at least three very distinct classes of salts,—the *metaphosphates*, which are monobasic; the *pyrophosphates*, which are bibasic; and the *phosphates*, which are tribasic. When a metaphosphate is heated with an excess of potash or soda, the acid is displaced or divided, and converted entirely into ordinary tribasic phosphate. Such is also the action of water at 536° F. In the presence of a monobasic metaphosphate, it intervenes as a base, completing the constitution of an ordinary tribasic phosphate.

The formula PO^{5}, RO therefore becomes $PO^{5}, 3RO$; but instead of a single salt of this form, there are produced thus—

$$6(PO^5\,RO)+12HO = PO^5,3RO + 3PO^5,\ RO,\ 2HO + 2PO^5,3HO$$

In two of these salts, the fixed base and the water act the same part, the acid in the one being united to 3 atoms of base, in the other to 3 atoms of water.

It is remarkable, that whilst the substances contain 6 atoms of base, each capable of uniting with 2 atoms of acid, and, as it might be supposed, ready to seize upon it, the mineral base should only take 1 out of 6 atoms of acid, leaving two to the water and dividing the other 3 with it. To judge from the result, one might be led to say, that at 536° F. water acts as a base with more energy than the mineral bases themselves.

The pyrophosphates, which are bibasic, undergo an analogous change, that is to say—

$$2(PO^5,2RO) = PO^5,3RO + PO^5,\ RO,\ 2HO$$

The water therefore unites with the mineral base in order to furnish the 6 atoms of base required for the formation of the two new salts.

It is clear that we should change nothing in the general expression of these facts, if we said that the hydrogen of the water acts as a metal, instead of saying that the water acts as base. We shall not therefore stop to dilate upon this point of view.

It must nevertheless be observed, that in such experiments the part played by the water does not always appear so simple; more obscure affinities are sometimes manifested, which give rise to more numerous and complicated bodies. Thus—

Bromide of cyanogen and water furnish hydrobromate of ammonia and carbonic acid; sulphocyanide of potassium gives bicarbonate of potash and hydrosulphate of sulphuret of ammonium; the cyanides of mercury and silver give carbonate of ammonia and reduced metal.

These reactions, which are frequently the last terms of a series of transformations of which the intermediate ones have disappeared, are very simply represented if we no longer regard water as a compound acting *en masse*, but as a source of oxygen and hydrogen, which can present either the one or the other in a nascent state. The formation of carbonic acid and ammonia in the presence of carbon and nitrogen is then no longer astonishing, and may be readily explained and foreseen.—*Comptes Rendus*, March 7, 1853, p. 411.

On the Action of Sulphuretted Hydrogen on Picric Acid.
By M. Aimé Girard.

The action of sulphuretted hydrogen on picric acid has never been studied; it was just noticed by Riecker, who announced that it gave rise to the formation of a yellow acid, confusedly crystal-

lized, and soluble in water, alcohol and æther; but the researches of this chemist stopped here. I have taken up this investigation, and arrived at the result, that sulphuretted hydrogen exerts the same action upon picric acid that it does in general upon organic substances in which nitrogen exists in the state of hyponitrous acid, namely, the elimination of oxygen to form water and fixation of hydrogen—a decomposition which is attended by a deposit of sulphur.

When a cold saturated alcoholic solution of picric acid is saturated with ammonia, and sulphuretted hydrogen is then passed into it until saturation, the liquid acquires a very intense red colour, and deposits a mass of small deep red crystals. When the alcoholic liquid is distilled, sulphur is deposited, and a fresh quantity of red crystals is obtained. This substance contains ammonia. Treated with acetic acid, an acid crystallizes from it in beautiful red needles; with nitrate of silver it gives a brick-red precipitate. The analysis of these two bodies gave the following numbers:—

1. *Acid.*

	I.	II.	III.	IV.	Average.		Calc.
C	35·76	35·50	35·46	35·7	35·6	12	36·1
H	2·65	2·73	2·82	2·9	2·7	5	2·5
N	21·50	21·42	21·48	21·4	21·4	3	21·1
O	40·09	40·35	40·24	40·2	40·2	10	40·3

2. *Silver Salt.*

	I.	II.	III.	Average.
AgO	37·4	37·6	37·1	37·4
Acid	62·6	62·4	62·9	62·6

These numbers give the formula $C^{12} H^5 O^{10} N^3$ for the acid, and $C^{12} H^4 AgO^{10} N^3$ for the silver salt. This latter formula might be written $C^{12} H^4 O (NO^4)^2 N, AgO$; and the acid, which is consequently monobasic, will be $C^{12} H^4, O (NO^4)^2 N, HO$. It is clearly 1 equiv. of picric acid, $C^{12} H^3 O^2 (NO^4)^3$, in which 1 equiv. of hyponitrous acid is destroyed, 4 equivs. of oxygen eliminated, and 2 of hydrogen fixed, according to this equation—

$$C^{12} H^3 O^2 (NO^4)^3 + 6HS = C^{12} H^5 O^2 (NO^4)^2 N + 4HO + 6S.$$

This acid consequently belongs to the series of bodies discovered by M. Zinin, including naphthalidame, nitrobenzamic acid, &c. I propose to call it *picramic acid.*

Picramic acid is obtained by precipitating a hot aqueous solution of the ammoniacal salt with acetic acid. After a little time, very brilliant needles of a ruby-red colour are deposited. They are four-sided prisms, beviled at the extremities, and grouped in the rhomboidal system. Sometimes these needles are attached to one another, forming tables, so that the acid may appear under two different forms. When powdered, its colour is a dull orange-red. It is soluble in alcohol; nearly insoluble in water, even when boiling; soluble in æther, from which it crystallizes in well-defined rhombohedra. It has great colouring power; its cold saturated alcoholic solution is

red. It has only a slightly bitter taste. When heated, it undergoes no alteration at 212° F.; at 329° F. it fuses, and crystallizes on cooling. At an elevated temperature, it is decomposed, disengaging tarry fumes and leaving a residue of coal. Hydrocyanic acid and ammonia exist in the products of decomposition. Thrown upon red-hot charcoal, it fuses and burns briskly, leaving a coaly residue. A drop of ammonia added to the alcoholic solution produces a red tint of remarkable intensity.

Treated with sulphuric acid, it dissolves with a red colour; if this solution be diluted with water, and ammonia added to it drop by drop, the picramic acid is precipitated in needles without alteration; an excess of ammonia then redissolves it with the usual red colour. The action of muriatic acid is the same. Hot concentrated sulphuric acid decomposes and carbonizes it. Concentrated nitric acid decomposes it with an abundant disengagement of nitrous fumes; the fluid becomes straw colour; and the acid, becoming oxidized, returns to the state of picric acid.

Picramate of ammonia, dissolved in water and treated with a current of chlorine, deposits a pulverulent yellow substance, which is insoluble in water, but soluble in alcohol, from which it is deposited with a resinous aspect. Picramic acid combines readily with bases, and generally gives crystalline salts.

Picramate of Potash, $C^{12} H^4 O (NO^4)^2 N, KO$, is obtained crystallized by precipitating the ammoniacal salt by potash whilst hot; it is deposited on cooling in elongated, rhomboidal, transparent, red tablets. These are tolerably soluble in water, but dissolve in alcohol with difficulty. When heated, they undergo no alteration, except at a high temperature; they then detonate slightly, leaving a carbonaceous residue. The potash was determined in the state of sulphate, by calcining the salt with a little sulphuric acid. The calcination must be very gently managed, to avoid projection. Analysis gave—

	Found.	Calculated.
Potash	19·9	19·8
Acid	80·1	80·2

Picramate of Ammonia, $C^{12} H^4 O (NO^4)^2 N, NH^3$.—This is the substance obtained by the action of sulphuretted hydrogen on picrate of ammonia. When directly prepared, by dissolving picramic acid in alcohol, saturating it with ammonia, and leaving the solution to spontaneous evaporation, it appears in rhombohedric prisms of a very deep orange-red colour. These crystals are soluble in water and alcohol, but insoluble in æther. The alcoholic solution is of a fine red colour. Submitted to long boiling in water, it is decomposed, depositing a brown powder. Heated to 212° F., it undergoes no alteration. At 275° F. it effloresces, with loss of ammonia; at 329° F. it fuses; at a more elevated temperature it is decomposed. In the analysis the nitrogen was determined by volume. This gave in 100 parts—

	Found.	Calculated.
Nitrogen.....	26·9	27·0

Picramate of Baryta, $C^{12} H^4 O (NO^4)^2 N, BaO$.—When picramate of ammonia is precipitated by nitrate of baryta with heat, this salt is deposited in little silky tufts of red gilded needles. It is soluble with difficulty both in water and alcohol. Heated to 392° F., it undergoes no alteration; at a higher temperature it detonates, leaving a carbonaceous residue. The baryta was determined in the form of sulphate. Analysis gave—

	Found.	Calculated.
Baryta	27·9	27·8
Acid	72·1	72·2

Picramate of Copper, $C^{12} H^4 O (NO^4)^2 N, CuO$, is an amorphous yellowish-green precipitate, insoluble in water and alcohol, soluble in acids and in ammonia. It detonates slightly. Analysis gave—

	Found.	Calculated.
Oxide of copper.....	17·2	17·3
Acid	82·8	82·7

Picramate of Lead is obtained by double decomposition in the form of an orange powder. It is soluble in water, insoluble in alcohol, and soluble in ammonia and in acids. When heated, it explodes; it also detonates by a violent blow, but without much noise. It leaves a carbonaceous residue.

Picramate of Silver, $C^{12} H^4 O (NO^4)^2 N, AgO$, is a completely amorphous red precipitate. It contains no water. It is insoluble in alcohol and cold water; treated with boiling water, it is decomposed, leaving an insoluble residue. When heated, it becomes decomposed and blackened at about 284° F.; the residue fuses at 329° F. Thrown on red-hot charcoal, it burns, but without detonation. This salt does not become black in the light. Analysis:—

	Found.	Calculated.
Oxide of silver	37·6	37·6
Acid	62·4	62·4

The soluble picramates give no precipitate with salts of manganese, iron, cobalt and nickel; with the salts of mercury they give a red precipitate, like hydrated peroxide of iron; the precipitate is soluble in acids.—*Comptes Rendus*, March 7, 1853, p. 421.

Crayons for writing on Glass. *By* R. Brunnquell.

The author prepares crayons for writing on glass, so as to enable the contents of glass vessels to be described immediately upon them in the following manner:—4 parts of spermaceti (or stearine), 3 parts of tallow, and 2 parts of wax are fused in a cup; 6 parts of minium and 1 part of potash are then stirred into it, the mass kept warm for half an hour, and then poured into glass tubes of the thickness of a lead-pencil. After rapid cooling, the mass may be screwed up and down in the tube, and cut to the finest point with a knife. A crayon is thus obtained which will readily write upon clean dry glass.—Dingler's *Polytech. Journ.*, vol. cxxvii. p. 236.

Upon the Combinations of Boracic Acid and Water with Baryta, Strontia and Magnesia. By Prof. H. Rose.

A. Equivalents of chloride of barium and neutral borate of soda were dissolved each in 12 parts of water, and the solutions mixed cold. In order that the solution of borate of soda may be free from carbonic acid, it is boiled for a time, and then allowed to cool in a closed vessel. The precipitate, originally free from carbonic acid, is very soluble in water. It was dried, without washing, between blotting-paper. In this manner

The neutral salt $BaO\,BO^3 + 3HO$ was obtained. The analysis of this salt, dried at 212° F., gave the following composition :—

		Oxygen.		
Baryta	57·35	6·00	3	59·90
Boracic acid.....	26·98	18·55	3	27·31
Carbonic acid	6·08	4·44	1	5·74
Water	7·34	6·52	3	7·05
Chloride of sodium	2·25			

The salt $4BaO\,BO^3 + CO^2 + 7HO$ is obtained when the above solutions are mixed hot and boiled for some time. The quantity of water contained in this salt, which, although it was precipitated hot is greater than in the salt precipitated in the cold, is however not sufficient to constitute $BaO, BO^3 + 2HO$.

As in the analogous lime compound, some boracic acid, although only a small quantity, is extracted by the action of the hot water. When, therefore, neutral compounds are precipitated from the salts of the alkaline earths by neutral borate of soda, just as by the neutral carbonates of the alkalies, they resist the action of cold, but not that of hot water. In consequence of the solubility of the compound, especially in hot water, very dilute boiling solutions could not be employed.

B. For the following experiments, solutions of common borax in 12 parts of water, and an equivalent proportion of chloride of barium in the same quantity of water, were employed.

The salt $5(BaO + 2BO^3 + 2HO) + BaO, HO + HO$ is contained in the precipitate which results from the mixing of the above fluids when cold. The precipitate is not washed, but dried between blotting-paper. The filtered solution still gives a precipitate with borax. Analysis of the precipitate, dried at 212° F.—

		Oxygen.		
Baryta	47·07	4·92	3	50·12
Boracic acid.....	37·90	26·06	5	38·08
Water	12·47	11·08	6	11·80
Soda.....	0·18	0·05		
Chloride of sodium	2·38			

The same salt remained when the preceding precipitate had been washed several weeks with water, by which it was much diminished in quantity. There always remain traces of chlorine in it, and the salt has attracted carbonic acid. Analysis of the salt, dried at 212° F.—

		Oxygen.		
Baryta	48·41	5·06	3	50·12
Boracic acid	35·55	24·46	5	38·08
Carbonic acid	4·02	2·90		
Water	12·02	10·68	6	11·80

The same salt was also thrown down when the two solutions were mixed in such proportions that the chloride of barium remained in excess in the solution. Analysis gave results similar to the preceding. When the precipitate had been heated to 392° F., it had the following composition:—

		Oxygen.		
Baryta	53·24	5·56	6	52·72
Boracic acid	39·76	27·34	10	40·05
Water	7·00	6·22	7	7·23

The compound was then exposed to a temperature of 572° F. By this it lost 9·01 per cent. of water, and then had the composition—

		Oxygen.		
Baryta	55·39	5·79	6	55·60
Boracic acid	41·37	28·45	10	42·22
Water.....	3·24	2·78	2	2·18

The compounds obtained are consequently—

$5(BaO+2BO^3+2HO)+BaO\,HO+HO$ at 212°.
$5(BaO+2BO^3+\ HO)+BaO\,HO+HO$ at 392°.
$5(BaO+2BO^3)\quad +BaO\,HO+HO$ at 572°.
$5(BaO+2BO^3)\quad +BaO$, or more correctly $3BaO+5BO^3$ at a red heat.

The boracic salts of baryta resemble those of lime. They contain however more water.

The compound which contains 3 atoms of baryta to 5 atoms of boracic acid is very stable, although not absolutely so; by long washing it takes up a little carbonic acid; it has a somewhat varying composition, according as it has been obtained by an excess of borax or of chloride of barium, as is shown by the following compositions of the anhydrous compounds:—

	I.	Oxygen.	II.	Oxygen.
Baryta.....	56·47	(5·90)	57·85	(6·04)
Boracic acid	43·53	(29·25)	42·15	(29·00)

In the first experiment an excess of borax, in the second an excess of chloride of barium was employed. Both precipitates were produced by cold solutions, and sufficiently washed with cold water. The compound obtained by an excess of borax agrees with the composition $3BaO+5BO^3$ better than that produced by an excess of chloride of barium; for, in another investigation, instituted at another time, a borate of baryta obtained by means of an excess of borax in cold solution, showed the following to be its composition in the anhydrous state:—

		Oxygen.
Baryta.....	56·60	5·92
Boracic acid	43·40	29·84

C. In the following experiments, solutions of common borax and chloride of barium in 12 parts of water were again employed. They were however mixed whilst boiling. The precipitate thus obtained, when dried at 212° F., consisted of—

		Oxygen.		
Baryta	49·93	5·22	3	50·12
Boracic acid.....	36·49	25·10	5	38·08
Water	12·38	11·00	6	11·80
Chloride of sodium	1·02			
Chloride of barium	0·18			

The compound, heated to 392° F., lost 6·14 per cent. of water, and had then essentially the following composition:—

		Oxygen.		
Baryta	53·75	5·62	3	53·27
Boracic acid	40·30	27·72	5	40·47
Water	5·95	5·29	3	6·26

Heated to 572° F., the borate of baryta lost 9·98 per cent. of water, and had then the following composition:—

		Oxygen.		
Baryta	56·04	5·86	3	55·58
Boracic acid.....	42·04	28·91	5	42·24
Water	1·92	1·70	1	2·18

At a boiling heat somewhat more boracic acid is expelled by water than in the cold.

Boracic Acid, Water and Strontia.—The solution of borax behaves with salts of strontia nearly in the same manner as with salts of lime, as somewhat more boracic acid is separated at an elevated temperature than at the ordinary temperature of the atmosphere.

A. In these experiments, common borax and chloride of strontium, dissolved in equivalent proportions in 12 parts of water, were employed. Mixed cold.

The salt $7SrO+3BO^3+4HO$ is the precipitate thrown down by the mixture of the above-mentioned solutions, when merely pressed, without washing, between filtering-paper, and dried at 212° F. The fluid filtered from this salt still gives a precipitate with borax. Analysis of the salt, dried at 212° F.—

		Oxygen.		
Strontia	37·58	5·82	3	39·50
Boracic acid.....	44·43	30·56	5	44·45
Water	15·39	12·68	7	16·05
Soda.....	0·27	0·07		
Chloride of sodium	2·33			

If the compound be heated to 392° F., it loses 8·10 per cent. of water, and has then, not taking the other salts mixed with it into consideration, the following composition:—

		Oxygen.	
Strontia	41·32	6·39	3
Boracic acid.....	51·64	35·51	5
Water	7·04	6·26	3

At 572° F. the salt loses water, and has the following composition :—

		Oxygen.	
Strontia	42·67	6·60	3
Boracic acid	53·33	36·68	5
Water	4·00	3·55	$1\frac{3}{4}$

These strontia salts have probably the following composition :—

$5(SrO+2BO^3+2HO)+SrO\,HO+3HO$ at 212° F.
$5(SrO+2BO^3+\ HO)+SrO\,HO$ at 392° F.
$5(SrO+2BO^3+\frac{1}{2}HO)+SrO\,HO$ at 572° F.
$5(SrO+2BO^3)+SrO$, at a red heat, or more correctly $3SrO+5BO^3$.

B. The same solutions as before were mixed while boiling, and kept at that heat for some time. The precipitate, pressed between blotting-paper and dried at 212° F., had the following composition :—

		Oxygen.		
Strontia	38·70	5·99	2	3
Boracic acid	40·91	28·13	3	or 5
Water	16·84	14·96	5	8
Chloride of sodium..	1·70			
Chloride of strontium	1·85			

	Calculated.			
Strontia	3 at.	38·61	2 at.	40·84
Boracic acid....	5 at.	43·45	3 at.	41·37
Water	8 at.	17·94	5 at.	17·79

From this the author concludes, that the solution of neutral borate of soda behaves towards the alkaline earths like those of the neutral carbonates of the alkalies, except that the precipitated borates are hydrated, whilst the corresponding carbonates are anhydrous. The solution of common borax does indeed throw down acid salts, but these do not contain the quantity of acid corresponding with the biborate of soda; they are salts which must be regarded as combinations of biborates with the hydrates of the same bases. Water does not expel so much boracic acid as carbonic acid.

A. *Boracic Acid, Water and Magnesia.*—Equivalent proportions of neutral borate of soda and sulphate of magnesia were dissolved in 12 parts of water, the solution of the former boiled for a considerable time, and allowed to cool in a closed vessel before being used. The solutions were mixed cold, the precipitates washed and dried at 212° F. Analysis gave :—

		Oxygen.		
Magnesia	36·82	14·72	22	36·48
Soda	7·94	2·04	3	2·75
Boracic acid	29·24	20·11	10	28·92
Water	26·00	23·11	36	26·85

The compound dried at 212° had attracted no carbonic acid. It is therefore probable that this precipitate is only a mixture of biborate of soda with a very basic borate of magnesia—a mixture (at

212° F.) of 3(NaO 2BO^3 5HO) with 4(MgBO^3 HO) and 18MgO HO. In the ascertained composition there would then only be 1 atom of water too little. In another preparation, the quantity of magnesia was quite different,—26·22 magnesia, 24·16 boracic acid and soda, and 27·62 water.

The greater part of the borate of magnesia was dissolved in the fluid which was filtered from the precipitate just described. It gave a strong precipitate on being heated, which was filtered whilst hot, and washed with hot water until the washing-water no longer gave the reaction of sulphuric acid.

The compound, dried at 212° F., contained some carbonic acid. Its composition was as follows:—

		Oxygen.		
Magnesia	51·46	20·57	26	51·36
Soda	6·29	1·61	2	6·15
Boracic acid	16·96	11·66	5	17·22
Carbonic acid ..	2·52	1·84	1	2·17
Water	22·77	20·24	26	23·10

The soda here is united with the boracic acid, and indeed, as the salt attracts carbonic acid during its drying, probably as neutral borate of soda. If 2NaO BO^3 + 3MgO BO^3 HO is contained in the precipitate, there remain still 23 atoms MgO HO. Thus by the action of a boiling heat, the boracic acid is expelled by the water from the greater part of the borate of magnesia.

On a repetition of the same experiment, a totally different result was obtained; consequently the composition of the precipitate is not constant:—

Magnesia.....	38·60
Boracic acid and soda.....	32·43
Carbonic acid	5·43
Water	23·54

B. *Precipitations with common Borax at an elevated temperature.*—Solutions of equivalent proportions of sulphate of magnesia and borax in 12 parts of water were mixed by adding the sulphate of magnesia to the borax. By boiling, some more of the precipitate was thrown down. Altogether, however, the quantity was about seven-eighths of the magnesia employed. After drying at 212° F., the compound contained some carbonic acid. Analysis gave—

		Oxygen.		
Magnesia	41·82	16·72	10	42·15
Soda	11·05	2·84	2	13·12
Boracic acid	21·89	15·05	3	22·03
Sulphuric acid ..	1·53	0·92		
Carbonic acid ..	0·77	0·56		
Water	22·94	20·40	12	22·73

This salt, if we may suppose that the boracic acid is contained in it either as common or as neutral borate of soda, consists therefore essentially of hydrate of magnesia, mixed with biborate (or neutral borate), sulphate, and carbonate of soda, which must have lost

nearly all their water by drying at 212° F., and of a little borate of magnesia. It is, moreover, to be observed, that neutral borate of soda, like common borax, only loses half its water at 212° F. The former consequently still contains 4 atoms of water, and the latter 5 atoms, at 212° F.

It is remarkable, that borate of magnesia can be deprived of nearly the whole of its boracic acid by hot water, combining with water, and depositing hydrate of magnesia. The affinities however are different at other temperatures, and at the ordinary temperature the separated boracic acid unites with the precipitated magnesia to form borate of magnesia and a double salt of borate of magnesia and borate of soda.—Poggendorff's *Annalen*, lxxxvii. p. 1.

On the Preparation of the Tannic Acids. By B. Sandrock.

The author finds, as was previously the case with Mohr, that the directions for the preparation of the tannic acids, given in the sixth edition of the Prussian Pharmacopœia, are injudicious. According to the Pharmacopœia, the tannic acids are to be extracted by means of an æther to which a tenth part of water has been added. Sandrock, on the contrary, recommends the method originally adopted by Pelouze, of employing common crude æther, instead of pure or watery æther, in the extraction of the gall-nuts; for if pure or watery æther be employed in the displacement, the solution of pure tannic acid in æther, which forms the lower stratum of the fluid, is so thick that it can scarcely flow, in some cases clogging the cotton used for closing the funnel to such an extent as to put a stop to all passage. In consequence of this also the quantity of pure tannic acid obtained is generally very small.

The operation is more readily effected, however, when crude æther is employed, because the small quantity of alcohol contained in this renders the thick under stratum of solution of tannic acid more fluid; in this manner it has the consistence of almond-oil. Instead of crude æther, a mixture of 16 parts of æther with 1 part of alcohol may be employed. The fluid still separates into two strata, and these are readily parted mechanically by means of a separating funnel. The tannic acid obtained by the evaporation of the lower layer is perfectly free from impurities. The upper layer contains the gallic acid and colouring matter of the galls, together with tannic acid. If æther be employed, to 8 parts of which 1 part of alcohol is added, the fluid still separates into two layers corresponding with the above; but the lower one is smaller, and the upper one contains considerably more tannic acid than in the former case, and these proportions go on increasing in proportion to the increase in the quantity of alcohol, as the author ascertained by several experiments. Lastly, if much more alcohol be employed, as 4 parts of æther and 1 part of alcohol, a fluid is obtained which does not separate into two strata, which contains all the tannic and gallic acids and colouring matter, and from which these foreign matters cannot be so readily separated from the tannic acid.

By the process just described more tannic acid is always obtained than in operating with pure or watery æther, although a certain quantity of it is dissolved in the upper stratum. This can also be recovered by evaporating the fluid to dryness, or distilling off the æther, and treating the residue with pure æther until the lower layer of the solution no longer appears green. This is to be separated, filtered if necessary with the addition of a little alcohol, and evaporated; in this manner a sufficient quantity of useful tannic acid is obtained to repay the trouble of the operation.

The prescription given by Mohr for the preparation of tannic acid, according to which the galls are to be treated with æther and alcohol, the decanted fluid, which does not separate into strata, evaporated, and the residue regarded as tannic acid, is rejected by the author, for the product contains all the gallic acid and colouring matter of the galls, which otherwise are contained in the upper layer of the ætherial extract.—*Archiv der Pharm.*, cxxii. p. 265.

On Phycite, the Saccharine Matter of Protococcus vulgaris. *By* M. Lamy.

The author has discovered two proximate principles in the *Protococcus vulgaris*, of which one is remarkable for the beauty of its crystals and its saccharine taste. He calls it *phycite*. The following is a summary of his recent researches upon this substance.

1. The elementary composition of phycite is as follows:—

Carbon	39·33
Hydrogen	8·25
Oxygen	52·46

which is represented by the formula $C^{12} H^{15} O^{12}$, in consequence of its relations—

$$C^{12} H^{15} O^{12} = C^{12} H^{12} O^{12} + 3H = C^{12} H^{14} O^{2} + H.$$

Phycite. Glucose at 212°. Mannite.

2. It crystallizes with very great facility in perfectly transparent prisms, belonging to the right rectangular prismatic system, but with anomalies of development which still remain to be explained.

3. It forms no definite combinations with bases or chloride of sodium.

4. It is not changed by potash, and only reduces the blue solution of tartrate of potash sulphate of copper and potash with great difficulty; but it is actively attacked by nitric acid, which gives rise to the same products as with the sugars.

5. It does not ferment with beer-yeast.

6. It has no action on polarized light.—*Comptes Rendus*, April 11, 1853, p. 655.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Cobalt. *By* E. FREMY.

IN this memoir the author shows that cobalt is further removed from iron and chromium on the one hand, and from nickel on the other, than has hitherto been generally supposed.

Protoxide of Cobalt, CoO.—Solutions of protoxide of cobalt give with potash and soda rose-red precipitates, which have hitherto been regarded as pure hydrates of protoxide of cobalt. The author found that potash is always contained in this precipitate. The hydrate of protoxide of cobalt, when it is dissolved and then reduced in a stream of hydrogen for the determination of the cobalt, always gives an excess, in consequence of its containing alkali. The reduced cobalt renders reddened litmus-paper blue.

Deutoxide of Cobalt, $Co^3 O^4$.—Rammelsberg has already shown that an intermediate oxide of the formula of magnetic oxide of iron must lie between the protoxide and the peroxide. Fremy has confirmed this assertion; he found that nitrate of the protoxide of cobalt, when heated to redness over a spirit-lamp, left such an oxide, which according to its analysis contained 26·8 per cent. of oxygen. The precipitate thrown down by an excess of potash from a cold solution of a salt of the protoxide of cobalt, acquired a brown colour in the course of several months when placed in an apparatus filled with oxygen. It had been converted into a hydrate of the above oxide, of the formula $Co^3 O^4$, 7HO, and contained 16·4 per cent. of oxygen and 35·8 per cent. of water.

The following are descriptions of combinations of cobalt resulting from the action of ammonia upon salts of this metal*.

According to the observations of Fremy, the phænomena which are exhibited during the action of ammonia upon salts of cobalt are very complicated. The concentration of the fluid, the access of the air, the kind of salt with which one operates, all have an influence on the result.

1. When soluble salts of cobalt, such as the acetate, sulphate or muriate of protoxide of cobalt, dissolved in a large quantity of water, are decomposed by ammonia, the fluid first acquires a green or blue colour; it then becomes turbid and completely decolorized, whilst basic salts of cobalt separate in the form of green precipitates.

* See the articles on these subjects by Genth, Claudet and Fremy, which have appeared during the last few years, Chem. Gaz., vol. ix. pp. 165, 230, 286; and vol. x. pp. 95, 424.

If the ammonia has not been added in too great a quantity, the filtrate frequently no longer contains any trace of cobalt.

2. *Ammonio-cobaltic Salts.*—If cobalt salts be treated with an excess of ammonia with exclusion of the air, double salts of ammonia and protoxide of cobalt are formed, which are generally of a pale rose colour and beautifully crystallized. These salts absorb oxygen, with the acquisition of a brown colour; they are decomposed by pure water, furnishing green basic salts. The author calls these salts *ammonio-cobaltic salts* (*sels ammonia-cobaltiques*).

3. *Superoxidized Ammonio-cobaltic Salts* (*sels ammonia-cobaltiques suroxygénés*).—The author gives this name to another class of salts, which are produced when a salt of cobalt dissolved in ammonia is exposed to the air. These fluids acquire a brown colour, and their acid is then saturated with bases consisting of oxygen, hydrogen, nitrogen, and an oxide of cobalt. Under these circumstances ammonia has the property of inducing the formation of an oxide of cobalt, for the salts contain the elements of ammonia and the two oxides $Co^2 O^3$ and CoO^2 in various proportions according to the mode of treatment, so that the following four series of salts, differing among themselves, are produced, namely—

A. *Oxycobaltia salts* (*sels d'oxycobaltiaque*). B. *Luteocobaltia salts* (*sels de lutéocobaltiaque*), which are formed from the salts of series A, when these are decomposed by pure, or, which is better, acidulated water. C. *Fuscobaltia salts* (*sels de fuscobaltiaque*), which are produced when ammoniocobaltic salts have been exposed to the air for a considerable time, when they become brown. D. *Roseocobaltia salts* (*sels de roséocobaltiaque*), which are formed when ammoniacal solutions of cobalt salts are decomposed by an excess of ammoniacal salt in the presence of the air. These salts have a more or less red or rose colour.

I. *Ammoniocobaltic Salts.*

Several salts of this series have already been prepared by H. Rose, by passing ammoniacal gas over powdered salts of cobalt. Fremy has prepared these same salts and other new ones in a different manner, namely by causing a solution of ammonia to act upon the salt of cobalt.

These salts are soluble without decomposition in watery ammonia. In contact with pure water they are decomposed; ammonia is set free and a basic salt separated, which scarcely contains any ammonia. If this decomposition be effected with boiled water and in the absence of air, a bluish basic salt of the protoxide of cobalt is the result; in aërated water, on the contrary, the basic salt has a greenish colour, and then contains, together with the protoxide of cobalt, the oxide $Co^3 O^4$.

Nitrate of Ammoniocobalt (*azotate ammoniacobaltique*), $CoO, NO^5, 3NH^3, 2HO$.—To a concentrated solution of pure nitrate of cobalt, of the composition $CoO, NO^5, 5HO$, an excess of ammonia is added in the absence of air. The blue precipitate first produced is again dissolved by an excess of alkali. The fluid becomes of a

wine-red colour, and rose-coloured crystals of nitrate of ammoniocobalt soon separate.

The salt is very quickly washed with liquid ammonia, and dried first between blotting-paper, and afterwards *in vacuo*. It acquires a brown colour when exposed to the air. It is rose-coloured and perfectly inodorous. Water decomposes it, setting free ammonia; basic nitrate of oxide of cobalt is precipitated. This green salt however is again dissolved in the ammoniacal fluid, which acquires a brown colour if exposed to the air. Alkalies disengage ammonia from the solution, with precipitation of hydrate of protoxide of cobalt. The salt is decomposed at once by heat, leaving a residue of deutoxide of cobalt, $Co^3 O^4$. Analysis gave:—

Cobalt	19·1	1	18·4
Nitrogen	36·1	1	35·0
Ammonia	31·6	3	31·8
Water	6·9	2	6·8

Muriate of Ammoniocobalt (*chlorure ammoniacobaltique*), $CoCl, 3NH^3, HO$, is produced by bringing together a concentrated solution of chloride of ammonium and liquid ammonia without access of air. A bluish precipitate is first formed, which rapidly dissolves in an excess of ammonia, forming a rose-coloured fluid. In a few days this solution deposits large, octahedral, nearly colourless crystals, which are to be rapidly washed with ammonia. In its general conduct towards water, ammonia and air, this salt is like the preceding. Analysis:—

Cobalt	24·1	1	24·2
Chlorine	30·0	1	28·3
Ammonia	40·8	3	40·8

Sulphate of Ammoniocobalt (*sulfate ammoniacobaltique*), $CoO, SO^3, 3NH^3$, which was obtained by H. Rose in the manner above described, could not be prepared in a crystalline form by the method adopted by the author. This salt is nevertheless formed when ammonia is allowed to act upon a concentrated solution of sulphate of cobalt in the absence of air. The solution is rose-coloured. Alcohol precipitates the salt from this solution, but it loses a portion of its ammonia during the process.

II. *Oxycobaltia Salts.*

These salts are produced when the preceding ammoniocobaltic salts are exposed to the air; at least the sulphate and nitrate are thus obtained. These salts separate in crusts from the solutions, which have become brown in the air. If the resulting salt is soluble, as is the case with the muriate, it cannot be prepared, because it changes in the solution even when evaporated *in vacuo*.

These salts are mostly olive-coloured; they are but sparingly soluble in ammonia; they are decomposed by cold, and still more rapidly by hot water, evolving pure oxygen gas, which produces an effervescence. During this decomposition the fluid becomes strongly ammoniacal, and a green basic salt separates having for its base the

oxide $Co^3 O^4$. This basic salt can be again dissolved under the influence of the air in the ammoniacal fluid, which thereby acquires a brown colour. The salts of this series may be distinguished from those of the other series by the possession of these properties.

Nitrate of Oxycobaltia (*azotate d'oxycobaltiaque*), $Co^3 O^4, 2NO^5, 5NH^3, 2HO$.—The concentrated solution of nitrate of ammoniocobalt, when exposed to the air, becomes covered with a crystalline layer, consisting of small, shining, brown prisms. These crystals, when dried *in vacuo*, often become green. The salt is deliquescent, and is decomposed by moist air.

Nitrate of oxycobaltia is soluble in warm liquid ammonia; it is deposited from this solution in prisms, which are often of considerable size. In pure water, even when cold, it undergoes the decomposition described above with evolution of oxygen, whilst basic nitrate of cobalt is deposited and ammonia set free. At 392° F. it is decomposed with a kind of detonation, leaving black oxide, $Co^3 O^4$. Sulphuric acid decomposes the salt in the cold, forming sulphate of ammonia and sulphate of protoxide of cobalt, with disengagement of oxygen gas, by measuring which the author was enabled to determine the proportion of oxygen which exists in the salt. Sulphurous acid decomposes the salt, becoming converted into sulphuric acid. Muriatic acid also decomposes it by heat, with disengagement of chlorine, forming protochloride of cobalt and muriate of ammonia. Sulphuretted hydrogen disengages oxygen, and gives a precipitate of protosulphuret of cobalt. Oxalic acid is not converted into carbonic acid; it disengages oxygen, and forms oxalate of cobalt. Cold watery solution of potash evolves oxygen, and forms first of all a brown fluid, from which protoxide of cobalt separates with the least heat; the base of this salt must consequently contain more oxygen than that oxide. Sulphuret of ammonium precipitates the salt of a black colour without appreciable disengagement of oxygen. Organic substances, such as alcohol and æther, have no action on the salt. Analysis gave—

Cobalt	20·2	21·7	19·2
Ammonia.....	27·0	28·5	26·8
Hydrogen	5·2	5·1	5·3
Oxygen	5·6		
Nitrogen	29·4	29·0	31·3

Sulphate of Oxycobaltia (*sulfate d'oxycobaltiaque*), $Co^3 O^4, 2SO^3, 5HO$.—In order to allow the formation of this salt to proceed slowly, so as to avoid the elevation of temperature which results from the combination of the ammonia with the salt of cobalt, and especially to prevent the action of too much oxygen at once upon the mixture, the liquid ammonia is put into a flask, and the crystals of sulphate of cobalt put into it, so that they may dissolve slowly in the ammonia, the flask being opened from time to time to replace with fresh air that which has been deprived of its oxygen. The salt separates at the surface of the fluid. It consists of olive-coloured prisms, which are not deliquescent; it is soluble in ammonia without de-

composition, like the preceding salt. Analysis gave 5·6 per cent. oxygen, 20·9 cobalt, 30·0 ammonia, 28·3 sulphuric acid.

Muriate of Oxycobaltia (*chlorhydrate d'oxyco.*) is formed by exposing the muriate of ammoniocobalt to the air. The fluid rapidly absorbs oxygen, and becomes brown. If it be now saturated with muriate of ammonia, the salt separates in small yellow prisms. This salt has always a certain quantity of luteocobaltia mixed with it.

III. *Luteocobaltia Salts.*

These salts are formed,—1st, when dilute solutions of salts of ammoniocobalt are exposed to the air; 2ndly, when crystallized salts of oxycobaltia are treated with a small quantity of water, crystals of this series separate then from the brown fluid; 3rdly, when the brown solutions produced by the action of an excess of oxygen upon the salts of ammoniocobalt are treated with dilute acids; 4thly, when salts of roseocobaltia are boiled with ammonia.

The salts of this series, as their name implies, are frequently of a fine yellow colour; they crystallize readily, possess considerable stability, and resist the action of boiling water for some time. They may be purified by solution in boiling water and recrystallization, without undergoing decomposition. A boiling solution of potash decomposes these salts, with deposition of hydrate of the sesquioxide of cobalt, Co^2O^3, HO, and evolution of ammonia. Dilute acids precipitate them from their watery solutions in a crystalline form.

These salts are decomposed by heat; ammonia is evolved, and the residue consists of sesquioxide of cobalt, Co^2O^3, and a cobalt salt.

Potash and soda furnish no precipitate; but if the solution be heated to boiling, sesquioxide of cobalt is separated and ammonia evolved. Ammonia gives no precipitate. Alkaline phosphates and carbonates produce no precipitate. Ferrocyanide of potassium forms a yellow non-crystalline precipitate. Iodide of potassium gives a yellow precipitate. Chloride of platinum produces a yellow crystalline precipitate. Sulphuret of ammonium gives a black precipitate. No precipitate is produced by sulphuretted hydrogen.

If sulphate of luteocobaltia be treated with baryta, luteocobaltia is set free; it is soluble, of a fine yellow colour, strongly alkaline, and only decomposable with evolution of ammonia when exposed to the action of heat.

Nitrate of Luteocobaltia, $Co^2O^3, 3NO^5, 6NH^3$, is formed,—1st, by the exposure of a dilute solution of nitrate of ammoniocobalt to the air; 2ndly, by the decomposition of nitrate of oxycobaltia with water; 3rdly, by the repeated decantation of the fluids from which nitrate of oxycobaltia has been previously deposited and separated.

This salt crystallizes in small golden-yellow tablets, and may be recrystallized from pure water, which only dissolves it in small quantity. Long exposure to the action of boiling water partially decomposes it, producing a brown colour. When heated, it is immediately decomposed with a sort of detonation; it then evolves reddish fumes, ammonia and water, leaving a residue of sesquioxide

of cobalt. It is thrown down from its watery solution by acids. Analysis yielded:—

			Calculated.	
Cobalt	16·9	18·0	2	17·0
Ammonia	28·7	30·0	6	29·3
Nitrogen	35·4	36·3	3	36·3
Hydrogen	5·8	5·5	1	5·1

Sulphate of Luteocobaltia, $Co^2 O^3, 3SO^3, 6NH^3, 4HO$, is of a fine orange-yellow colour; it exhibits the general properties of the nitrate; it is sparingly soluble in cold, more readily in boiling water, from which it again crystallizes on cooling. Analysis gave—

Cobalt	17·3
Ammonia	29·9
Sulphuric acid	35·2

Muriate of Luteocobaltia, $Co^2 Cl^3, 6NH^3$, is formed in regular octahedra of a beautiful red colour when an ammoniacal solution of chloride of cobalt is exposed for about a month to the air; or with more certainty when the oxygenated solution of chloride of ammoniocobalt is treated in the cold with an excess of muriatic acid, or with powdered muriate of ammonia. In the latter case it forms small yellow crystals.

This salt dissolves slowly in cold water; it is decomposed by hot water. Analysis gave—

		Calculated.
Cobalt	22·8	22·0
Chlorine	38·5	39·7
Ammonia	36·5	38·1
Hydrogen	7·2	6·7

IV. *Fuscobaltia Salts.*

These are uncrystallizable salts, which are produced by exposing ammoniacal solutions of cobalt to the air, when they acquire a brown colour, or by the decomposition of salts of oxycobaltia by means of water. All these salts are decomposed by boiling their solutions; ammonia is evolved, and hydrate of the sesquioxide of cobalt deposited. Potash and soda give no precipitate with solutions of these salts; on the application of heat, ammonia is evolved, and hydrate of the sesquioxide of cobalt deposited. Sulphuric and nitric acids give a precipitate, which is at first yellow, but becomes rose-coloured by boiling, from the formation of salts of roseocobaltia. Muriatic acid produces protochloride of cobalt, with disengagement of chlorine. Muriate of ammonia by boiling furnishes a crystalline precipitate of muriate of roseocobaltia. Ferrocyanide of potassium gives a brownish-yellow precipitate; phosphate of soda, a brown precipitate; iodide of potassium, none. Chloride of platinum gives a brownish-yellow precipitate.

Nitrate of Fuscobaltia, $2(Co^2 O^3, NO^5), 5NH^3, 4HO$.—This is decomposed by heat with a sort of detonation, even before attaining a red heat. Analysis gave—

			Calculated.
Cobalt	28·2	..	29·8
Nitrogen	22·2	..	24·8
Ammonia	20·3	21·3	21·5
Hydrogen	4·6	5·2	4·8

Granular Nitrate of Fuscobaltia, $Co^2 O^3, 2NO^5, 4NH^3, 3HO$, is thrown down when a solution of nitrate of ammoniocobalt, which has been standing in the air for two or three months, is heated with nitrate of ammonia; it is in the form of a brown granular salt. Analysis gave—

			Calculated.
Cobalt	19·7	..	20·6
Ammonia	25·7	23·7	23·7
Nitrogen	30·6	..	29·4
Hydrogen	4·4	..	5·2

This salt, like the preceding, appears to result from the combination of ammonia with a basic nitrate of sesquioxide of cobalt, which in this case is $Co^2 O^3, 2NO^5$.

Sulphate of Fuscobaltia, $Co^2 O^3, 4NH^3, 2SO^3, 4HO$.—When a stream of ammonia is passed through a solution of sulphate of cobalt exposed to the air, this salt is thrown down in the form of a brown resinous substance. It is also obtained by precipitating with a few drops of alcohol a solution of the salt of ammoniocobalt which has been exposed to the action of the air during several days. This salt dissolves in water with a brown colour. When heated, it evolves ammonia and oxygen, leaving a residue of sulphate of protoxide of cobalt. Analysis gave—

			Calculated.
Cobalt	23·6	21·8	22·1
Sulphuric acid	31·5	..	30·0
Ammonia	25·6	..	25·5

Muriate of Fuscobaltia, $Co^2 Cl^2 O, 4NH^3, 3HO$, is produced when the chloride of ammoniocobalt is exposed to the air. It becomes brown, and when evaporated *in vacuo* gives a viscous and uncrystallizable residue. If the brown solution be precipitated by alcohol and dried *in vacuo*, the salt is obtained in the solid state. It may perhaps result from the combination of 4 equivs. of ammonia with 1 equiv. of sesquichloride of cobalt, in which the third equivalent of chlorine is replaced by 1 equiv. of oxygen. According to this view, one can understand how this salt may be formed, when the ammoniacal solution of chloride of cobalt is exposed to the action of oxygen, and also how this muriate of fuscobaltia, in the presence of muriatic acid or muriate of ammonia, can produce new salts containing the elements of ammonia and of the sesquichloride of cobalt, $Co^2 Cl^2 O, 4NH^3 + HCl, NH^3 = HO + Co^2 Cl^3, 5NH^3$. The salt $Co^2 Cl^3, 5NH^3$ is the compound which will be hereafter described as muriate of roseocobaltia. The analysis of muriate of fuscobaltia gave—

			Calculated.
Cobalt	25·8	25·5	25·3
Ammonia	28·0	28·0	29·1
Chlorine	32·3	..	30·4
Hydrogen	6·0	..	6·4

Granular Muriate of Fuscobaltia, $Co^3\ ClO^3, NH^3, 5HO$, is formed when a solution of chloride of ammoniocobalt, which has been exposed for two or three months to the air, is boiled with muriate of ammonia; a rose-coloured salt first separates, which belongs to the following series, and afterwards a black crystalline salt. This latter is soluble in cold water, to which it gives a dark brown colour; muriate of ammonia throws it down from this solution. No precipitate is produced in the solution of this salt by nitrate of silver in the cold; whence the chlorine cannot be contained in it in the manner of an ordinary chlorine compound. Analysis gave—

		Calculated.
Cobalt	40·3 to 41·0	42·2
Chlorine	17·7 to 18·0	16·9
Ammonia	7·0	8·1

The author considers that this salt contains as its base an oxide of cobalt of the same formula as the magnetic iron ore, in which the fourth equivalent of oxygen has been displaced by chlorine, thus $Co^3\ ClO^3$.

V. *Roseocobaltia Salts.*

These salts are formed under various circumstances:—1. When salts of ammoniocobalt are exposed to the air. In this case, however, they are almost always mixed with salts of the preceding series. 2. When solutions of salts of ammoniocobalt, which have been exposed to the air, are slightly acidulated. 3. In the most simple manner, when solutions of salts of ammoniocobalt, which have been exposed to the air for two or three days, and which contain salts of fuscobaltia, are boiled with ammoniacal salts. 4. From salts of oxycobaltia, when these are brought into contact with ammoniacal salts. 5. Several others can be prepared by the double decomposition of a salt of roseocobaltia, as the nitrate from the muriate by means of nitrate of silver, the nitrate or the muriate from the sulphate by means of nitrate or muriate of baryta.

All these salts have a fine red colour; they are scarcely soluble in cold water, but more so in boiling water, which decomposes them with disengagement of ammonia and precipitation of sesquioxide of cobalt. Potash and soda disengage no ammonia from these salts in the cold, and only act upon them when the fluid is heated to boiling. Ferrocyanide of potassium gives a brownish-yellow precipitate. Alkaline phosphates and carbonates produce no precipitate. Muriatic, nitric, and sulphuric acids precipitate the salts in a crystalline state. Fixed bases decompose the salts of roseocobaltia in the cold, producing roseocobaltia, which is soluble in water. The author obtained the base by treating the sulphate with baryta-water. It has a rose colour, is strongly alkaline, and becomes decomposed by

boiling, with disengagement of ammonia and separation of sesquioxide of cobalt.

Nitrate of Roseocobaltia, $Co^2 O^3, 5NH^3, 3NO^3$, forms small, very shining crystals, scarcely soluble in water, and which are decomposed by boiling water, with evolution of ammonia and deposition of sesquioxide of cobalt. When heated, it is immediately decomposed with detonation. Analysis gave—

		Calculated.
Cobalt	18·0 to 19·0	17·9
Ammonia	25·3 to 26·6	25·8
Nitrogen	32·6	34·0
Hydrogen	4·7	4·5

Acid Sulphate of Roseocobaltia, $Co^2 O^3, 5NH^3, 5SO^3, 5HO$, has a strongly acid reaction, and is readily soluble in water, which thereby acquires the red colour of peroxide of mercury. Iodide of potassium and chloride of platinum produce a yellow, and ferrocyanide of potassium a greenish-yellow precipitate with this salt. Phosphate of soda gives no precipitate. The salt dissolves in water without decomposition. If this solution be heated after the addition of ammonia, two salts are formed, namely, neutral sulphate of roseocobaltia and sulphate of luteocobaltia. Analysis :—

		Calculated.
Cobalt	14·9	14·3
Sulphuric acid	48·3	48·4
Ammonia	20·9	20·6

Neutral Sulphate of Roseocobaltia, $Co^2 O^3, 3SO^3, 5NH^3, 3HO$, crystallizes in beautiful, transparent, quadratic prisms, and is but slightly soluble in water. Analysis furnished—

		Calculated.
Cobalt	17·3 to 18·7	18·6
Ammonia	..	27·0
Sulphuric acid	37·0 to 38·3	38·1
Hydrogen	6·2	5·7

Muriate of Roseocobaltia, $Co^2 Cl^3, 5NH^3, HO$.—This salt is the product of the decomposition of all peroxidized salts of ammoniocobalt with muriatic acid. It was first observed by M. Deherain, working in the author's laboratory, and led the author to undertake this investigation of cobalt. It is readily obtained when the chloride of ammoniocobalt is exposed to the air for two or three days. When the fluid has become dark brown, it is boiled with muriate of ammonia; it disengages oxygen in abundance, and the salt separates in a crystalline form and of a rose colour. Heated in a current of hydrogen, this salt leaves a residue of pure cobalt; it may consequently be employed in the preparation of pure cobalt. When heated, it disengages ammonia, muriate of ammonia, water and a gas, which appears to consist of nitrogen and hydrogen. Analysis gave—

		Calculated.
Cobalt	22·6	22·8
Chlorine	40·9	41·0
Ammonia	30·1	32·8
Nitrogen	26·2	27·0
Hydrogen	6·4	6·1

Hydrate of Sesquioxide of Cobalt, $Co^2 O^3$, HO, separates from the peroxidized ammoniacal salts when their solutions are boiled with alkalies. The hydrate gave on analysis 65·3 per cent. of cobalt; the anhydrous oxide, 27·9 per cent. of oxygen. It always contains a trace of the alkali by which it was precipitated.

TABLE OF THE NEW COMPOUNDS.

1. *Salts of Ammoniocobalt, containing the Protoxide.*

Nitrate	$CoO, NO^5, 3NH^3, 2HO$.
Sulphate	$CoO, SO^3, 3NH^3$?
Chloride	$CoCl, 3NH^3, 3HO$.

2. *Salts of Oxycobaltia.*

Nitrate	$2(CoO^2, NO^5), 5NH^3, 2HO$.
Sulphate	$2(CoO^2, SO^3), 5NH^3, 3HO$.

3. *Salts of Luteocobaltia.*

Nitrate	$Co^2 O^3, 3NO^5, 6NH^3$.
Sulphate	$Co^2 O^3, 3SO^5, 6NH^3, 4HO$.
Muriate	$Co^2 Cl^3, 6NH^3$.

4. *Salts of Fuscobaltia.*

Nitrate	$Co^2 O^3, 2NO^5, 4NH^3, 3HO$.
Sulphate	$Co^2 O^3, 2SO^3, 4NH^3, 4HO$.
Muriate	$Co^2 Cl^2 O, 4NH^3, 3HO$.

5. *Salts of Roseocobaltia.*

Nitrate	$Co^2 O^3, 3NO^5, 5NH^3$.
Sulphate	$Co^2 O^3, 3SO^3, 5NH^3, 3HO$.
Muriate	$Co^2 Cl^3, 5NH^3, HO$.

Ann. de Chim. et de Phys., 3rd series, vol. xxxv. p. 257.

Examination of a natural Product recently imported from America, and formed in part of Crystallized Borates of Soda and Lime. *By* M. LECANU.

This substance appears to exist in considerable quantities in Iquiqua, a dependency of the Republic of Ecuador. The author found it to consist of—

Water	34·60
Earthy matters	10·70
Chloride of sodium	9·87
Sulphate of soda	5·04
Borate of soda	13·44
Borate of lime	26·35

The latter borate, moreover, exists in it crystallized in four-sided prisms, which distinguishes it from the pulverulent borate of lime, the only form of that mineral hitherto discovered in nature.

If this product really exists in sufficient quantities to be profitably worked in the localities indicated, it is clear that the borate of soda contained in it, and the boracic acid of both its borates, might be extracted for commercial purposes; or its borate of lime might be converted into borate of soda by double decomposition. Its discovery would then present considerable interest in a commercial point of view.—*Comptes Rendus*, March 28, 1853, p. 580.

On the Anhydrous Acids. By L. Chiozza.

Having continued the study of the action of oxychloride of phosphorus upon the salts of several monobasic acids, I have succeeded in preparing some new anhydrous acids in a state of purity, which appear to me to possess considerable interest.

Anhydrous Caproic Acid presents itself under the form of a limpid oil, very similar in its physical characters to anhydrous caprylic acid. When recently prepared, its odour is not disagreeable, and becomes aromatic by heat; when exposed to moist air, it rapidly becomes hydrated, and evolves the fœtid odour of ordinary caproic acid. Its composition is represented by the formula—

$$C^{12}H^{22}O^3 = \left\{\begin{matrix} C^6H^{11}O \\ C^6H^{11}O \end{matrix}\right\} O.$$

Anhydrous Angelic Acid was prepared, like the preceding, by the action of oxychloride of phosphorus on the potash salt. It is also a neutral, uncrystallizable oil, becoming slightly acid by distillation; its odour has no resemblance to that of hydrated angelic acid. Its transformation into hydrated acid is effected with great difficulty by simple contact with water, but alkaline solutions effect it in a few minutes. Its analysis gave numbers agreeing with the formula—

$$C^{10}H^{14}O^3 = \left\{\begin{matrix} C^5H^7O \\ C^5H^7O \end{matrix}\right\} O.$$

I have also obtained in a pure state the *angelate of benzoyle*—

$$C^{12}H^{12}O^3 = \left\{\begin{matrix} C^5H^7O \\ C^7H^5O \end{matrix}\right\} O,$$

the physical characters of which are identical with those of the substance previously described.

The action of potash in small quantity upon anhydrous angelic acid is very curious, and presents an apparent anomaly. If a few grammes of this substance, which is perfectly neutral with test-papers, be heated with a small morsel of caustic potash, there is immediately a formation of angelate of potash and of free hydrated angelic acid, which reddens litmus-paper strongly. This reaction is explained by the following formula:—

$$\left\{\begin{matrix} C^5H^7O \\ C^5H^7O \end{matrix}\right\} O + \left\{\begin{matrix} K \\ H \end{matrix}\right\} O = \left\{\begin{matrix} C^5H^7O \\ K \end{matrix}\right\} O + \left\{\begin{matrix} C^5H^7O \\ H \end{matrix}\right\} O$$

I have also ascertained that the experiment succeeds equally well with the other anhydrous acids.

Anhydrous Nitrocinnamic Acid is remarkable for the facility with which liquid ammonia splits it exactly into nitrocinnamide and nitrocinnamate of ammonia. This property has enabled me to obtain pure nitrocinnamide, the preparation of which by means of nitrocinnamic æther requires considerable time. The anhydrous acid is a resinous substance, which is very sparingly soluble in æther, and becomes hydrated very rapidly.

I may be allowed, in concluding this note, to call the attention of chemists to a fact which appears important in a theoretical point of view, namely, the conversion of acids into aldehydes by means of the corresponding chlorides.

I have already shown that chloride of cumyle is quickly attacked by potassiocumyle, and that the product of this reaction consists of chloride of potassium and cumyle—

$$C^{10} H^{11} O$$
$$C^{10} H^{11} O.$$

Now it is evident that by replacing the metallic combination of a radical by a metallic hydruret, the hydruret of the radical, that is to say its aldehyde, must be obtained. The experiment succeeds very well with the hydruret of copper, discovered by M. Wurtz, and the chloride of benzoyle. As soon as these two substances are brought into contact, the reaction commences with evolution of heat, and the product contains essence of bitter almonds. The following equation will render this double decomposition intelligible :—

$$CuH + Cl(C^7 H^5 O) = CuCl + (C^7 H^5 O)H.$$

Comptes Rendus, April 4, 1853, p. 630.

On the Preparation of Lithia from Triphylline.
By Hugo Müller.

Triphylline, which occurs with beryl, tourmaline, columbite, and zwieselite in a very coarse-grained vein-granite on the Rabenstein near Zwiesel in Bavaria, is, on account of the large quantity of lithia contained in it and its solubility in acids, the best material for the preparation of this rare alkali. For this purpose I employ the following process, which possesses many advantages over those hitherto adopted.

The mineral, coarsely pounded, is dissolved in concentrated muriatic acid, with gradual addition of nitric acid; the solution obtained, which must contain all the iron as peroxide, is poured away from the insoluble residue, which usually consists of felspar, beryl and mica; it is then evaporated to dryness, with constant stirring, and the dry mass heated until all free acid is evaporated. The somewhat hygroscopic mass which remains is finely powdered and boiled with water, and the solution filtered off. If the operation has been well performed, and all the iron changed into peroxide, the

solution contains no trace of that metal, but only the chlorides of lithium, manganese and magnesium; for in proportion as the acid which held the phosphate of iron in solution was driven off, this substance was precipitated in the form of a heavy white powder. As this precipitate is very dense, it is readily separated by filtration and washed. To separate the manganese and magnesia from the lithia, the solution is mixed with freshly-prepared hydrate of lime in excess, and boiled with access of air until the separated hydrate of the protoxide of manganese has become more highly oxidized. The brown precipitate, besides the manganese and excess of hydrate of lime, also contains the magnesia* and any phosphoric acid which may be present in the solution. All the lithia remains in the solution; this is filtered off, and the dissolved lime precipitated by a mixture of caustic ammonia and its carbonate. It is again filtered and evaporated, and the chloride of lithium which remains heated in a porcelain crucible to fusion. It still contains a small quantity of chloride of sodium, which however is sufficient to change to an orange-red the characteristic deep crimson colour which is communicated to flame by pure lithia. This chloride of sodium may be removed by Rammelsberg's method, in which the mass is macerated with a mixture of alcohol and æther, which dissolves the chloride of lithium, but leaves the chloride of sodium undissolved.

To obtain perfectly pure lithia, it is best to change the crude chloride of lithium into the carbonate, by dissolving the former salt in the smallest sufficient quantity of caustic ammonia, and laying small pieces of carbonate of ammonia in the solution, which is to be kept as cool as possible. Warmth, and especially a boiling heat, would again change the carbonate of lithia and chloride of ammonium into chloride of lithium and carbonate of ammonia. The carbonate of lithia, which has been thrown down in the cold, is placed upon a filter, and washed with alcohol, by which the chloride of sodium is got rid of.—*Ann. der Chem. und Pharm.*, lxxxv. p. 251.

Method of obtaining positive Protographic Impressions directly upon Plates of any description, especially on those intended for Engraving. By A. Martin.

The method employed by the author is the same as that which he described for taking positive pictures on glass. The metallic plate, covered in the usual manner (but upon both sides) with etching-ground, is first coated with iodized collodion, then dipped in the solution of nitrate of silver, &c. The picture, when taken, is freed from the unmodified iodide of silver by the bath of cyanide of silver, washed with water, immersed in a solution of dextrine, and dried. The engraver may then make the same use of the design that he does of the outline, which is usually transferred to the etching-ground. A second impression on glass will preserve the design, which the operation of engraving will destroy upon the plate.

* Magnesia usually exists only in very small quantity in triphylline, and appears not to belong to this mineral itself, but rather to some of those with which it is associated.

Impressions taken in this way upon varnished metallic plates of any kind, or even upon cardboard, unite with the qualities of positive impressions upon glass, a strength and facility of transport of which the latter are deficient. The method is also applicable to wood-blocks.—*Comptes Rendus*, April 18, 1853, p. 703.

On the Combinations of Boracic Acid and Water with Metallic Oxides. *By* H. Rose.

Of these boracic acid compounds, only those precipitates were submitted to examination which were obtained by means of solution of biborate of soda in solutions of the sulphates of the oxides mentioned.

The *borate of cobalt*, which results from the action of cold solutions of equivalent proportions of borax and sulphate of cobalt, is not completely insoluble in water; the washing water consequently acquires a reddish colour, and becomes turbid on the addition both of borax and of sulphate of cobalt. After washing with cold water, it contains a very small quantity of sulphuric acid, but no soda; and when dried at 212° F., it has essentially the composition—

$$2CoO\,(BO^3\,HO)+CoO\,HO+HO.$$

The *borate of nickel* has a similar composition, except a difference in the quantity of water, when precipitated in the same manner and washed with cold water. When dried at 212° F. its composition is $2(NiO, BO^3\,HO)+NiO, HO+2HO$. If, however, the precipitate be not washed, but merely pressed between blotting-paper after filtering, it consists essentially of borate of nickel, NiO, BO^3+2HO, so that thus a third of the boracic acid is extracted by washing with cold water. If the solutions of the salts be mixed together whilst hot, and the whole kept for some time after mixing at a boiling heat, the precipitate, if it be not washed, but immediately after filtration pressed between blotting-paper, contains only half as much boracic acid, compared with the oxide of nickel, as the precipitate which is obtained from the cold solutions.

The precipitate of *borate of zinc* is also, like the nickel compound, essentially a neutral salt when the solutions of sulphate of zinc and borax have been mixed whilst cold, and the precipitate has not been washed after filtration, but merely dried between blotting-paper. After washing with cold water, it has essentially the composition $4(ZnO, BO^3\,HO)+5ZnO\,HO$. There is thus a considerable quantity of boracic acid extracted from the borate of zinc, considerably more than from borate of nickel under similar circumstances. If the solutions be mixed with one another whilst boiling, and the whole kept at that temperature for some time, the precipitate, when not washed, but merely pressed after filtration between blotting-paper, is of the same composition, but mixed with $2(ZnO)^3\,SO^3$ and a little sulphate of soda.

The *borate of cadmium* is not a perfectly neutral compound when obtained from cold solutions of sulphate of cadmium and biborate of soda, not washed after filtration, but merely dried between blotting-

paper, but contains a little more boracic acid, so that a small quantity of oxide of cadmium combined with boracic acid to form $CdO,2BO^3$, is contained in the precipitate. But if the solutions be mixed together whilst boiling, and the precipitate not washed, but only pressed between blotting-paper, it contains much less boracic acid, and consists essentially of $2(CdO,BO^3\,HO)+CdO\,HO$, but contains, besides sulphate of soda, more sulphuric acid in the form of insoluble basic sulphate of cadmium, so that the greater part of the hydrated oxide of cadmium is perhaps contained in the precipitate in this compound.—*Bericht der Berlin Akad.*, 1852, p. 614.

ANALYTICAL CHEMISTRY.

New Method of Analysis for the Organic Poisons.

By C. Flandin.

The author commences by laying down the principles on which he supposes the action of poisons may be explained:—1. Poisons are unassimilable substances. 2. They pass into the organism by absorption. 3. Their action is that of presence.

If these principles be correct, it follows that all poisonous substances, *whatever they may be*, must be found in the organs with which they have been brought into contact, or to which they have been transported by absorption. In the case of the inorganic poisons, experience has shown that there is no exception to the rule. It still remains to be shown that the same rule applies to the organic poisons.

Christison* states, with regard to opium, that as a general rule the medical jurist can scarcely obtain satisfactory proof of the existence of this substance *by the best methods of analysis at present known.* Now the best methods of analysis known at present for ascertaining the presence of opium, and of the organic proximate principles in general, consist in treating the suspected substances either with acetic acid or alcohol, filtering the liquid, and evaporating it to the consistence of an extract. This extract is then redissolved in water, either pure or acidified, and decolorized by animal charcoal, or the animal matters are precipitated as far as possible by various reagents (such as subacetate of lead, sulphuretted hydrogen, nitrate of silver, &c.). Lastly, the extractive matter thus obtained is tested by different reagents, such as nitric acid and perchloride of iron, when it is desired to ascertain the presence of morphine, the active principle of opium. In this way, however, no satisfactory results can be obtained. The poison is not isolated; it is not directly acted upon by the reagents; its characteristic properties consequently cannot be ascertained.

The author considers that animal substances may be divided as follows:—1. Proteine or albuminous substances. 2. Colouring matter. 3. Fatty substances.

* Treatise on Poisons, p. 697.

The proteine substances are readily coagulable, and in this state they become insoluble in water, alcohol, acids, &c.

The coloured or colouring matters are easily changed by various acids and alkaline agents, anhydrous lime and baryta for instance, without mentioning heat.

The fatty substances are separated with ease from all the other matters by alcohol and æther.

Now if an inorganic substance be mixed with organic substances, there is nothing more easy than to discover it. The organic substance is burnt, the inorganic principle is brought to the state of a soluble compound within the cinder, and then extracted with water. The process of carbonization or incineration by means of sulphuric acid for the discovery of the mineral poisons is founded on these very simple data.

But if the substance which it is necessary to separate from animal matters be combustible, or capable of essential modification by heat, the course is not so clear. The following is the process proposed:—

To 100 parts of the substance to be examined, 12 parts of anhydrous lime or baryta are to be added, and the whole pounded together in a mortar. The mixture is then to be heated to 212° F., then pulverized, either with the pestle, or with a special apparatus appropriated to this operation, which is very essential; the powder is to be treated with boiling anhydrous alcohol three times, filtering the liquid after cooling. This liquid as it leaves the filter is scarcely coloured; it only contains the proximate principle or principles sought for with the fatty or resinous matters.

The alcohol is now slowly evaporated, and the dry residue treated with æther to remove the fatty matters. If the principle be insoluble in æther (morphine, strychnine, brucine), it will be separated in the fluid, and may be obtained by filtration or simple decantation. If it be soluble in æther, the alcoholic residue or the ætherial fluid must be treated with a special solvent of the organic bases, such as acetic acid, precipitating the base afterwards by ammonia.

To 100 grms. of animal matter the author added a single grain or 0·05 grm. of morphine, strychnine and brucine; and by operating in the manner just described, succeeded in obtaining, in a state of absolute purity, a ponderable quantity of each of those principles. Instead of strychnine, morphine and brucine, the author employed crude opium, laudanum, decoction of nux vomica and of false angostura bark; and in these cases also he was able to isolate the poisonous principles. He also, in order to assure himself that his process was applicable to medico-legal purposes, poisoned animals with the smallest effective doses of the above-mentioned substances, when he was able to detect the poisons in the matters contained in the stomach and intestines, and sometimes even in organs to which they had been carried by absorption.

In one experiment, he mixed 2 grs. (or 10 centigrms.) of morphine with 100 grms. of flesh, leaving the substances to undergo putrefaction for two months. At the end of this period he discovered several centigrammes of morphine in the mass.—*Comptes Rendus,* March 21, 1853, p. 517.

New Method of determining the Value of Chloride of Lime. *By* Dr. Penot.

The most accurate method of determining the value of chloride of lime is that introduced by Gay-Lussac, and in which arsenious acid is employed; but the difficulty in recognising exactly the point when the sulphate of indigo added to the test-liquid becomes perfectly decolorized, renders the results uncertain to such a degree that there is a very general desire for a more practical and trustworthy process.

The method, introduced some years ago, based upon the reaction of chloride of lime upon protosulphate of iron, is known by every one who had followed it to be imperfect; for during the operation a quantity of chlorine is evolved and lost, and it is difficult to ensure the uniformity of the sulphate of iron.

The author therefore employs arsenious acid to determine the value of chloride of lime, and in such a manner that the moment at which a sufficiency has been added may be observed with the greatest accuracy. The method is based upon a well-known fact, which has already been taken advantage of for the purpose, though in a different manner, by Houton Labillardière.

When potato-starch is boiled in a solution of iodide of sodium, a colourless solution is obtained, which becomes blue on the addition of a minute quantity of acid or of chlorine.

In order to prepare a test-paper applicable to examination of chloride of lime, the author heats together—

1 grm. iodine,
7 grms. crystallized carbonate of soda,
3 grms. potato-starch,
¼ litre water,

until the liquid becomes colourless, when it is made up with water to 1 litre. White paper is then saturated with this liquid and dried.

The test-solution is prepared by dissolving 4·44 grms. of arsenious acid and 13 grms. crystallized carbonate of soda in about three-fourths of a litre of water, and then making up to exactly 1 litre. The use of hydrochloric acid, as in Gay-Lussac's method, must be avoided on account of its action upon the iodized paper.

To test a specimen of chloride of lime, 10 grms. are dissolved in a litre of water, an appropriate quantity is measured into a beaker, and the test-liquid added from a graduated glass until a drop of the liquid no longer produces a blue colour on the test-paper. This method gives directly the per-centage value of the chloride of lime, or the number of litres of chlorine to which a kilogramme is equivalent. In Gay-Lussac's method, this can only be determined by a table.

When it is desirable to have a control for the results obtained, the reverse experiment may be made by adding the solution of chloride of lime to a determinate volume of the test-solution until the liquid gives a blue colour to the iodized paper. Supposing that the chloride examined contains 90 litres of chlorine in the kilo-

gramme in the direct experiment, 90 measures will be necessary, and in the inverse one 111 measures.

It is easy to perceive when there is nearly enough of the test-liquid added, for then the test-paper is less strongly coloured, and the first drop in excess is sufficient to prevent the paper from altering any more.

When the value of the chloride of lime is very low, it is advisable to take only 10 measures of test-liquid, and add 90 measures of water. The result sought is then one-tenth of that found.

Bedles, in reporting upon the method proposed by Dr. Penot, expresses his opinion that it is far superior in practical value to any other.—*Bullétin de la Soc. Industr. de Mulhouse*, 1852, No. 118.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

Means of detecting the Dyes which have been used in the Dyeing of Stuffs.

It is not unfrequently desirable to know, with regard to a dyed stuff, in what manner it has been dyed, and what dyeing material has been employed. This cannot always be decided by the appearance; for example, in the case of a dark blue, the question rises whether the ground is pure indigo or pure logwood, or a mixture of both, or whether prussian potash-blue is not present, &c. For this purpose recourse must be had to chemical reagents.

In order to ascertain what mordants have been used, the most accurate method is to incinerate a sufficiently large piece of the stuff, and examine the ash.

Blue Colours.—These may consist of indigo, logwood, prussian blue or ultramarine.

Indigo-blue is fixed on cloth in various ways,—1st, in the blue vat; 2ndly, as so-called China or English blue, blue patterns upon a white ground, fixed, according to the principle of the blue vat, with lime and sulphate of iron; 3rdly, as pencil-blue, the indigo being deoxidized by means of oxide of tin and potash; and 4thly, as soluble indigo.

The first three blues are not acted upon by dilute acids or alkalies. By chlorine and nitric acid, on the contrary, they are destroyed. When the stuffs decolorized by chlorine are washed and dipped in a solution of logwood, the first two remain colourless because they contain no mordant, while the stuff dyed with pencil-blue becomes red on account of the tin which it contains.

The blue of soluble indigo, and that obtained with cyanide of potassium, agree in being destroyed by alkalies; at the same time, however, the blue of indigo leaves a white ground, while that of the cyanide leaves a rusty yellow ground on account of the iron mordant employed. In order to remove all doubt, a few drops of acidulated solution of cyanide of potassium should be added, which, if

iron is present, reproduces the blue colour. This confirmatory test should always be used in the case of green colours.

Prussian blue may be recognised by its being decolorized by alkalies, but not by chloride of lime, while the latter reagent destroys indigo-blue. The appearance alone is sufficient to indicate whether the blue is ordinary prussian blue or *bleu de France*, prepared with stannate of potash.

Logwood-blue may easily be recognised from the fact that it is destroyed by weak acids, and becomes red; in most cases this is a sufficient ground for inferring the presence of logwood, &c.

When the colour to be examined is a mixed one, for example, logwood-blue, with prussian blue or indigo, the colour of the logwood is first destroyed by dilute acid, the stuff washed, and treated with chlorine to ascertain whether the ground-colour is indigo or prussian blue.

Ultramarine may usually be recognised by its peculiar tint; after incinerating the stuff, it remains unaltered in the ash. Hydrochloric acid decomposes it, disengaging at the same time an unpleasant odour of sulphuretted hydrogen. When the ultramarine is imprinted with varnish, the stuff must be moistened with æther before the hydrochloric acid will act.

Red Colours.—With the exception of safflower, the red colouring matters require a preparation of alumina or tin.

Safflower may be easily recognised by its colour being discharged by caustic potash or soda. Madder colours, when treated with hydrochloric acid, acquire a yellow or orange tint without any shade of puce; upon then being treated with milk of lime, the colour becomes violet at those places where the hydrochloric acid has acted. The violet is permanent, and by boiling with soap, passes into rose colour.

The madder-red colours are less susceptible of alteration by acids the more they have been brightened by soap and the higher the temperature at which this took place. The great durability of the Turkish red is owing to this fact.

The red and rose colours from madder are separable into several kinds,—Turkish-red and rose, ordinary madder-red and rose, the true topical red, and the colours from garancine and garanceux.

Turkish-red may be known by its brightness and indestructibility by acids. Ordinary madder-red, when brightened, scarcely differs in any particular from a true topical colour. The only difference is in the mode of preparation. As the topical colour is prepared before printing with tin, and after printing the stuff is steamed, the white is somewhat yellowish, and becomes coloured in a decoction of logwood. The red and rose from garancine and garanceux differ from the above colours in not bearing brightening with soap, acids and alkalies. When treated with hydrochloric acid, they pass into orange, and do not then give a violet, but a dull blue colour, with milk of lime.

The tone of colour is sufficient to distinguish between colours produced from garancine or garanceux, the latter possessing an

orange shade. When the red is accompanied by violet, the distinction is still more easy, because garancine yields a violet, which is nearly as beautiful as that from madder, while the violet of garanceux is more reddish-gray.

The red colours from Brazil-wood and cochineal, when treated with hydrochloric acid and tin salt, become gooseberry-red; and then milk of lime produces a violet of little permanence, which disappears entirely on subsequent boiling with soap, while the madder colours acquire their greatest brilliancy by this treatment.

The red from cochineal differs from that of Brazil-wood in tone and in its behaviour with concentrated sulphuric acid; the former becomes bright cherry-red, the latter orange.

Yellow Colours.—The yellow of quercitron is discharged by chlorine and sulphurous acid, but it is not sensibly changed to orange by either caustic potash or tin salt.

The yellow of buckthorn-berries is likewise destroyed by chlorine; caustic potash renders it bright yellow. Heated with tin salt, it passes into orange; with sulphuric acid, it acquires a stone colour.

The orange and nankeen colours from fustic and fustet are changed to red by sulphuric acid; treated with potash, they acquire a colour resembling that of catechu; they are discharged by nitric acid.

The yellow from sumach acquires greater brightness with tin salt; with nitric acid, it becomes red; sulphuric acid does not produce much alteration; sulphate of iron changes it to gray.

The yellow from arnotto is but little affected by chlorine; concentrated sulphuric acid changes it to bluish-green; with nitric acid it assumes a darker colour, and then disappears entirely.

Chrome-yellow is unaltered by heating with weak hydrochloric acid, but destroyed by the concentrated acid. It is destroyed by caustic alkalies; boiling potash converts it into orange. Chrome-orange becomes greenish-yellow when treated with weak acids.

Black Colours.—Logwood-black contains iron as a mordant, sometimes iron and alumina. In the latter case it has a shade of blue. Such a colour is discharged by chlorine, a yellow resulting from the iron ground remaining. Treated with hydrochloric acid and tin salt, it becomes red, with the former more cherry-red, with the latter violet-red.

The blacks from astringent substances are easily recognisable by the shade of olive which they present. When treated with hydrochloric acid, they acquire a dull orange colour; tin salt dissolves the iron, and changes the colour to a dirty olive.

Chrome-black may be known by its behaviour with chloride of lime, which destroys the other kinds of black, while it changes chrome-black to a chestnut-brown.

The examination of mixed colours is somewhat more complicated; but as they are for the most part constituted of the substances already mentioned, it will not be difficult, by means of the above reactions, to ascertain in what manner and with what materials such colours have been produced.—*Beiblatt zur Deutsche Musterzeitung*, 1853, No. 1.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On a new Dye-Stuff from China. *By* Prof. W. Stein.

The author has investigated a dye-stuff which has been imported into Hamburg from China under the name of "Chinese yellow berries." Its yellow colouring principle is rutic acid. The dye-stuff itself does not consist of the berries of the plant, as implied by the name, but of a mixture of woody particles, namely of fragments of thin stalks and peduncles, generally deprived of their bark, together with unexpanded flower-buds. The colour of the flower portions is more or less pale yellow, often brown (from drying); that of the calyces, grayish brownish-yellow, often reddish at the base and brownish-green at the margins. On the upper portions of the latter, as well as on the leaves of the flower-buds, a granular coating is observed here and there by the lens; this appears like a resinous or waxy exudation, of a sulphur-yellow colour, often with a greenish or bluish-green tinge. When moistened with water, the coating becomes perceptible to the naked eye, whilst at the same time an odour reminding one of opium and saffron is evolved.

Botanical examination showed that the source of this substance must be a shrubby papilionaceous plant. The twigs are clothed with a smooth brownish-yellow bark, furnished with longitudinal striæ. Their woody portion, consisting of a light wood, is of a yellowish-white colour, and surrounds a pith of very close texture, of considerable size and of a light yellow colour. The inflorescence is in a loose raceme, as shown by the leaf-scars existing on the peduncles. The flowers appear to be on short stalks; the calyx is bell-shaped, coriaceous, wrinkled, striated at the base; its margin has five equal roundish teeth. The vexillum appears to be cordate, and the ten stamens to be monadelphous. The germen is furnished with bristles; the style crooked.

These vegetable matters, on treatment with æther in a displacement apparatus at the ordinary temperature, impart to it a fine chrome-yellow colour; chlorophylle, a fat which is readily saponifiable even in the cold and which evolves acroleine when heated, the peculiar odorous matter of the flowers, a brown bitter extractive substance, and the yellow colouring matter pass into solution.

The quantity of substance extracted by the æther after long-

continued action was 0·7 grm. from 20 grms., consequently 3·5 per cent. Extraction by alcohol of 0·811 in the same manner furnished 5·04, or 25 per cent. of extractive, consisting principally of colouring matter.

A portion boiled with 20 parts of water till the fluid was reduced to one-half, furnished a dark brown fluid, which on cooling deposited the colouring matter in greenish-yellow flakes; these in part attached themselves strongly to the sides of the vessel. Water extracted, besides the colouring matter, a gum which is precipitable by persulphate of iron and forms mucic acid when treated with nitric acid, traces of tannin and the above-mentioned extractive matter.

Starch could be recognised in the woody portions by means of iodine; an examination instituted with this view, showed that they, as well as the buds, contained the yellow colouring matter, but less of the brown extractive matter and gum.

In order to separate the yellow colouring matter in a pure state, the substance is repeatedly extracted with alcohol of spec. grav, 0·863. The greater part of the alcohol is then distilled off. The residue sets on cooling into a jelly, in consequence of the separation of the colouring matter in granular flakes; these are still rendered impure by the brown extractive matter and chlorophylle, and under the microscope appear to consist of agglomerations of prismatic crystals. The yellow matter is freed as much as possible from the extractive matter, which adheres to it obstinately, by repeated recrystallization from boiling water; the extractive matter, being equally soluble in cold and hot water, remains in the mother-liquor, and is finally got rid of by washing the colouring matter with cold water until this comes away colourless.

When purified as much as possible, the colouring matter possesses neither taste nor smell. Its colour, when dry, is pale yellow, with a slight mixture of green. The portions separated in flakes from a saturated boiling watery solution, on cooling from a saturated solution in boiling alcohol of spec. grav. 0·863, in a granular and sometimes also a globular form, consist, when viewed under the microscope, of very thin four-sided prisms. When heated dry, the yellow colour is heightened, owing to its at first acquiring a slight admixture of brown; fusion into a thin fluid soon takes place; the yellow colour afterwards becomes brown and the thin fluid thick, like sulphur. When the heat is continued, the mass at length puffs up, and ignites very readily in contact with the air, diffusing a remarkable odour of caramel. If the heating be effected in a test-tube, yellow fumes are produced, and a sublimate, consisting of a thickish fluid mixed with yellowish granules, is formed. It is sparingly or scarcely soluble in all the usual solvents, such as water, cold and boiling alcohol and æther; it is most soluble in alcohol of spec. grav. 0·863; the solutions have an acid reaction. The solubility of the colouring matter in water is greatly increased by alum, stannate of soda and acetic acid. A solution, saturated whilst boiling with the addition of alum, becomes of a pasty consistence on cooling. A solution, prepared in

the same way with stannate of soda, was of a greenish colour, and deposited nothing on cooling. A solution obtained by the addition of an equal volume of acetic acid of 65 per cent., $C^4 H^3 O^3 + HO$, to the water, was of a faint greenish colour, and on cooling deposited the colouring matter in flakes, which filled the entire fluid. The shade of colour of the material and of its solutions is changed by the alkalies, as well as by caustic baryta, lime and some acids, proto- and perchloride of tin, chloride of barium and salts of iron. A watery solution, prepared by boiling, which after cooling had scarcely any perceptible colour in a thickness of half an inch, immediately acquired a fine golden-yellow colour on the addition of a small quantity of a solution of alkali or alkaline earth. The same is the case with the dry colouring matter, which dissolves plentifully in such solutions; the solution, however, acquires a brownish-red colour. A small addition of muriatic acid renders the colour of the watery solution paler; a larger quantity produces the golden-yellow tint; the dry colouring matter immediately acquires a golden-yellow colour, as also does the alcoholic solution, from which, after long standing, a golden-yellow, or sometimes orange-coloured granular precipitate is deposited. Dilute sulphuric acid (1 : 3) behaves towards the watery solution in the same manner as muriatic acid; the yellow colour, however, is of a lower tint. Solution of alum acts in a similar manner to sulphuric acid; but the colour, after standing some time, becomes deeper. Solution of perchloride of tin, even in small quantity, produces the golden-yellow colour. Chloride of barium resembles perchloride of tin in its action; protochloride of tin acts like alum. Perchloride of iron in small quantity produces a yellowish-green colour, without precipitate; protosulphate of iron has a similar action, but the colour is lighter.

Baryta water and lime water produce precipitates of a beautiful orange or golden-yellow colour in the alcoholic solution. Precipitates are produced in the watery and alcoholic solutions by basic and neutral acetate of lead; these are partly of an orange and partly of a pure chrome-yellow colour. Sulphate of copper produces olive-coloured precipitates in these solutions.

The pure colouring matter appears to undergo no essential change by exposure to the air. When, however, it is dissolved in water in the presence of caustic ammonia, potash or baryta, it absorbs oxygen (0·05 grm. absorbed 0·5 cub. cent. in 12 hours; 1 cub. cent. in 48 hours), with the acquisition of a brown colour. At ordinary temperatures the change thus produced appears to be very slight; for such a solution, which was left standing over mercury until no further diminution of the volume of air resulted, still gave a yellow precipitate with solution of acetate of lead; the colour of the precipitate had only a trace of brown; the greater part at least of the colouring matter was separated by muriatic acid in beautiful golden-yellow flakes by a slight evaporation of the fluid. On the other hand, when the fluid is warmed at the same time that the absorption is going on, a complete alteration appears to take place; for a solution in baryta water, evaporated at 212° F., left behind a blackish-

brown residue, soluble in water, with the same colour; this solution gave a dingy olive precipitate with basic acetate of lead.

Nitric acid of the ordinary strength communicates a golden-yellow colour to the dry colouring matter, which passes rapidly into dark olive, and lastly into reddish-brown. When heated, nitrous acid is evolved, the evaporated fluid furnishes picric acid, and contains traces of oxalic acid.

The odour of caramel, diffused by the substance when heated to decomposition, shows that this body must be a saccharine compound. A solution of the colouring matter in caustic soda, mixed with solution of oxide of copper, and heated to boiling, only deposited a small quantity of protoxide of copper after long boiling. But when the colouring matter had been boiled with dilute sulphuric acid, the precipitate was rapidly and plentifully produced on the addition of caustic soda and oxide of copper, and heating the mixture.

When triturated with distilled sulphuric acid in the cold, a solution is produced, which is at first brownish-yellow, but afterwards becomes dark brownish-red; no sulphurous acid is set free. When this solution is heated, the evolution of formic acid is perceptible; this is afterwards accompanied by sulphurous acid. If the cold solution, after standing for about an hour, be diluted with water, olive-green flakes separate. But if the dilution with water be effected after a longer time, a violet precipitate is produced. The supernatant fluid is of a brownish-yellow colour; when the free sulphuric acid has been separated from it by carbonate of baryta, it gives on evaporation a blackish-brown fluid, from which are deposited crystals readily soluble in water.

The violet precipitate contains neither sulphur nor sulphuric acid; it is soluble in boiling alcohol, sparingly soluble in water, but dissolves in considerable quantity and with a yellowish colour in ammonia.

These properties of the colouring matter agree with those of rutic acid, first discovered in *Ruta graveolens* by Weiss, more closely examined and analysed by Bornträger, and since found by Rochleder and Hlasiwetz in capers. The result of the following analyses is the same. The acid contained 6·63 per cent., or 1 equiv. of water of crystallization, which was expelled at 212° F. The acid, dried at this temperature, gave—

Carbon	50·945	50·927	50·669	12	= 72	50·000
Hydrogen.....	5·592	5·527	5·516	8	8	5·550
Oxygen.....	43·463	43·546	43·815	8	64	44·459

The colouring matter crystallized from acetic acid contained, as shown by the following numbers, 1 equiv. less water, without any perceptible external change:—

Carbon	53·696	12 = 72	53·333
Hydrogen	4·903	7 7	5·185
Oxygen	41·401	7 56	41·481

Lead Salt, $C^{12} H^6 O^6 + 2PbO$.—Bornträger prepared a lead salt which contained 47·02 per cent. of oxide of lead, corresponding with

the formula $C^{12} H^6 O^6 + PbO$. Rochleder obtained a lead salt containing 44·62 per cent. of oxide of lead, for which he adopts the formula $(C^{12} H^8 O^8 + PbO) + 2(C^{12} H^7 O^7 + PbO)$. The author, although like Rochleder he precipitated a solution of the colouring matter in alcohol of spec. grav. 0·863 with a solution of acetate of lead in alcohol of the same strength, obtained a lead salt containing still more oxide of lead. This, when moist, was of a fine chrome-yellow colour, brownish-red when dry; in its preparation, the author mixed an excess of solution of acetate of lead with the solution of rutic acid. This compound contained 61·3 of oxide of lead. A salt of the composition $C^{12} H^6 O^6 + 2PbO$ ought to contain 59·59 per cent. of oxide of lead.

By frequently repeated precipitation of solutions of rutic acid with acetate of lead, there was first produced, on the addition of a small quantity of acetate, an orange precipitate, which only acquired a chrome-yellow colour on a further addition. Thus, in this case, compounds of different constitution are produced; the orange-coloured compounds contain more rutic acid. A chrome-yellow precipitate, triturated with rutic acid and alcohol, immediately changed its colour to orange. The excess of rutic acid was removed by washing with cold alcohol. By drying, the colour of the compound obtained in the manner just described passed into dark brownish-red, or nearly black. It contained 36·527 per cent. of oxide of lead. The orange-coloured compound was also produced by mixing a small quantity of acetate of lead with the solution of rutic acid. It contains 36·15 per cent. of oxide of lead. Lastly, it is also produced when the chrome-yellow compound is stirred with water to which a few drops of acetic acid have been added. The author considers that this precipitate may be a compound of rutic acid with bibasic rutate of lead. A compound of the formula $2(C^{12} H^8 O^8) + (C^{12} H^6 O^6 + 2PbO)$ would contain 35·1 per cent. of oxide of lead. Thus we have—

1. Crystallized acid, $C^{12} H^8 O^8 + HO$.
2. Dried at 212° F., $C^{12} H^8 O^8$.
3. Crystallized from acetic acid, $C^{12} H^7 O^7$.
4. In the bibasic salt, $C^{12} H^6 O^6, 2PbO$.
5. Rochleder and Bornträger's lead salt, $(C^{12} H^8 O^8) + (C^{12} H^6 O^6, 2PbO)$.
6. The author's second lead salt, $2(C^{12} H^8 O^8) + (C^{12} H^6 O^6, 2PbO)$.

Pure rutic acid, dissolved in boiling water with the addition of alum, communicates a fine sulphur-yellow colour to woollen stuffs, either with or without an alum mordant.

Experiments in dyeing with the Chinese "yellow berries" have shown that an agreeable yellow of various shades can be produced with it on wool and silk. The most advantageous process is to treat the stuffs with an alum mordant, and dye them whilst hot in decoction prepared with the addition of alum (1 oz. alum to 1 lb. of yellow berries). In this manner a citron-yellow colour with a tinge of green is obtained. This colour may be improved by cold washing with soap; hot soap-water changes it to an orange, which however

does not look well in consequence of a mixture of brown. By heating in water containing caustic ammonia, the colour loses its green tinge, and becomes fiery in consequence of a slight admixture of red. Caustic potash renders it brown; vinegar destroys this brown tint again. All these reagents at the same time extract some of the colouring matter from the dyed stuff.

By boiling with dilute sulphurous acid, the colour on the stuff is slowly bleached; still more rapidly with chloride of lime and the addition of an acid. The colour also fades very soon in the light, even without exposure to the direct action of the sun.

From these investigations we may conclude, that the "Chinese yellow berries" have no advantage as a dye-stuff over those already known to us, unless it be from the great quantity of colouring matter contained in them, which, as shown by experiment, amounts to between 20 and 25 per cent.—*Auszug aus dem Programm der Polyt. Schule zu Dresden*, March 1853.

Upon Oil of Cummin. By C. Völckel.

According to the previous investigations of Schweitzer and the author, oil of cummin is a mixture of an oil containing oxygen with one wanting that element. The latter (*carvene*), according to Schweitzer, has the same composition as oil of turpentine, and is obtained by the distillation of crude oil of cummin with powdered caustic potash or fused hydrate of phosphoric acid. The oil containing oxygen (*carvole*) is changed by this process into *carvacrole*.

In an earlier investigation, the author was unable, in consequence of operating only upon a small quantity of oil of cummin, to obtain carvole pure. He therefore, in the present case, endeavoured to obtain it from a larger quantity. Oil of cummin, as obtained by the distillation of cummin seed with water, acquires a colour by keeping. This coloration depends principally on the presence of a small quantity of a volatile substance, which moreover is readily changed by alkalies. To free the oil of cummin from this substance, it was mixed with half its volume of an alcoholic solution of caustic potash. A strong colour was immediately produced in this manner. After rather long action, which towards the end was assisted by slight heat, the oil of cummin was separated by water and distilled off with water. The residue was a soft, resinous, coloured substance, of which only a small quantity dissolved in caustic potash.

The oil of cummin thus purified is perfectly colourless, and has a much finer and more pleasant odour than in the crude state. It was purified from alcohol by washing with water, dried upon chloride of calcium, and distilled by itself in a retort with a thermometer inserted. The oil begins to boil at 347° F.; the boiling-point rises slowly at first, and the greater part of the oil distils over at 392° F. From this point the thermometer rises rapidly to 437° F.; the smaller portion of the oil passes over between 437° and 450° F. At this temperature a small quantity of a thick strongly-coloured oil remains in the retort.

As the boiling-points of the oil containing oxygen and of that free from this element lie rather wide apart (347° and 437° F.), their separation was attempted by simple distillation. This was effected in the following manner:—The intermediate distillate (with its boiling-point 392° to 437° F.) is first redistilled, when a portion of the oil goes over below 392° F., another between 392° and 437° F., and a small quantity from 437° to 446° F. In this manner the intermediate distillate may be more and more divided by repeated distillation. If the first distillate (boiling-point 347°–392° F.) be treated in the same manner, the oil of cummin is separated by many distillations into two principal portions. The greater part of it goes over completely at 347°–352° F., the smaller portion at 437°–446° F. A small quantity of oil was also obtained, the boiling-point of which was situated between these, but which, from its small quantity, could not be further separated.

The oil which passes over between 347°–352° F. has an odour like that of oil of cummin, but much finer and more pleasant. Its specific gravity is 0·861 at 59° F. In other respects it possesses the composition and properties ascribed by Schweitzer to carvene:—

Carbon	88·08	5 =	375	88·24
Hydrogen	11·87	4	50	11·76

The carvole, which passes over between 437° and 446° F., possesses an odour like that of the preceding oil. Carvole is decomposed in small quantity at every distillation; there always remains a small quantity of thick, strongly-coloured oil. This alteration in the carvole by heat is the cause of its rising boiling-point. This phænomenon is exhibited by very many oxygenized volatile oils with very high boiling-points.

In consequence of this change by heat, the complete combustion of carvole is difficult. If in an analysis it is burnt in a small bulb drawn out to a point, there is always a residue of coal in the bulb. This is the reason why less carbon was found in a former analysis of the portion of the oil of cummin, which passes over at 442° F., than in the following analyses: the carvole intended for analysis was weighed in a small glass tube, which was completely filled with oxide of copper when in the combustion-tube:—

Carbon	80·04	80·17	80·22	30 =	2250	80·00
Hydrogen	9·45	9·54	9·38	21	262·5	9·33
Oxygen	10·51	10·29	10·40	3	300	10·67

If this formula be compared with that of carvene, $C^5 H^4$ or $C^{30} H^{24}$, a close relation between them will be observed, 3 equivs. of hydrogen in carvene being replaced by 3 equivs. of oxygen in carvole. From this we may conclude that carvole is produced by the oxidation of carvene. But it is also possible that carvene has been formed from carvole by the displacement of the oxygen of the latter by hydrogen whilst in the plant.

Oil of cummin, obtained from cummin-seed of various years, contains these two oils in unequal quantity. The specific gravity of

carvole is greater than that of carvene, namely 0·953 at 59° F. Carvole is violently attacked by concentrated sulphuric and nitric acids, becoming resinous. According to Schweitzer, when repeatedly distilled with fused phosphoric acid or powdered caustic potash, it passes into carvacrole. This is also produced by the action of iodine upon oil of cummin and camphor. It is a thick fluid, with an odour like that of creosote, and dissolving like that substance in solution of potash; it is however distinguished from creosote by having a less specific gravity than water. According to Schweitzer, carvacrole consists of—

Carbon	82·20	82·84
Hydrogen	9·61	9·66
Oxygen	8·19	7·50

From this he calculates the formula $C^{26} H^{18} O^2$, which however expresses no relation between carvacrole and carvole or camphor, from which it is produced. The formula $C^{30} H^{20} O^2$ agrees pretty well with Schweitzer's second analysis, and appears to the author to be more correct than $C^{26} H^{18} O^2$. According to the formula $C^{30} H^{20} O^2$, carvacrole would consist of—

Carbon	83·33
Hydrogen	9·26
Oxygen	7·41

Its formation from carvole, $C^{30} H^{21} O^3$, would then be very readily explained, 1 equiv. of water being expelled by the action of phosphoric acid, iodine and caustic potash. The formation of carvacrole from camphor, $C^{10} H^8 O$, by means of iodine, is not less simple.

It appears that a small quantity of carvole passes over into carvacrole by mere heating to the boiling-point. The above analyses of carvole give a slight excess of carbon, which is readily explained if we suppose the formation of a small quantity of carvacrole during distillation.—*Ann. der Chem. und Pharm.*, vol. lxxxv. p. 246.

On the Distribution of Iodine. By Prof. Sigwart.

Professor Sigwart has ascertained the existence of iodine in the bituminous slate of the lias formation, which is so rich in organic remains, and also in the sulphurous springs of Wurtemberg. Iodine is contained in the water of Sebastiansweiler, in the sulphurous waters of Boll and Reutling, and in that of Balingen in larger quantity than in the brine of salt works.

This iodine is derived from the bituminous slate from which they arise. The author has consequently tested this slate for iodine.

No iodine could be discovered in the watery extract of 2½ oz. of finely-powdered slate from Boll. The slate was then completely carbonized in a retort at a red heat, and afterwards again treated with water. This watery extract, boiled down to a small quantity, exhibited no reaction upon starched linen with sulphuric acid and manganese. When however the linen had been taken out a con-

siderable time, and exposed to the air in a small glass with distilled water, a distinct reddening of the amylon took place. The carbonaceous residue of the slate was then completely reduced to ashes by a red heat, and again extracted with water. No iodine was to be recognised in this extract.

A more satisfactory result was obtained when a larger quantity of slate was mixed with soda-lime and carbonized in a retort.

But the most successful mode of showing the presence of iodine in the slate is to mix 15 oz. of powdered slate with a watery solution of chemically pure caustic potash, evaporating the mass to dryness, then destroying the bitumen by heating to redness in a retort, and washing the residue with water. This is filtered, the filtrate precipitated by alcohol, and the alcoholic fluid evaporated until a small quantity of watery fluid remains. Sulphuric acid is added to this until it has an acid reaction, and the turbid fluid is then allowed to stand twelve hours in an air-tight vessel, when it is poured away from the sediment and filtered. A strip of starched linen is introduced into this fluid, to which some manganese and a few drops of sulphuric acid are then added. Distinct reaction of iodine is immediately produced.—*Wurt. Naturw. Jahresbericht*, vol. xix. p. 43.

On Nitruret of Iron. By H. L. Buff.

Iron wire, heated to redness in a stream of ammoniacal gas, became brittle, crystalline and white, and acquired an addition of 6 per cent. to its weight. Heated to redness with soda-lime, it furnished ammonia. Chloride of iron, heated to redness in ammonia, furnished scales of tough metallic iron, containing 0·043 nitrogen. Iron reduced from oxide of iron precipitated by ammonia, by heating to redness in ammoniacal gas, contained 0·079 nitrogen. The same oxide of iron, heated to redness in a stream of oxide of carbon, contained 1·8 per cent. of carbon. This, heated to redness in a stream of ammonia, lost its deep black colour, and contained 1·159 nitrogen. The author considers that the quantity of nitrogen taken up by the iron depends upon the quantity of carbon contained in it. —*Ann. der Chem. und Pharm.*, vol. lxxxiii. p. 375.

On the Action of Ammonia on certain Metallic Arsenites. By M. Aimé Girard.

Those oxides which are soluble in ammonia are also soluble in that alkali when combined with arsenious acid; but these solutions do not all behave in the same manner.

Thus the arsenites of cobalt, nickel, and sesquioxide of iron dissolve readily in ammonia, especially when they have been recently precipitated; but in these cases no combination takes place between the ammonia and the arsenite; it is a simple solution, which after a certain time allows the arsenite to be deposited without having undergone any change. The arsenites of silver and copper are the only ones which give a very distinct reaction.

Arsenite of silver, when ammonia is poured over it, before it has become dull and granular, dissolves, furnishing a colourless liquid, from which, on the addition of alcohol, white transparent crystals are deposited at the end of a few days. These crystals are square tablets, grouped round a common centre. The salt is insoluble in water and alcohol, soluble in ammonia and nitric acid; the latter converts it into arseniate. Muriatic acid decomposes it, forming chloride of silver and arsenious acid, the latter being dissolved. Heated with potash, it disengages ammonia, and oxide of silver is precipitated. Heated to 212° F., it undergoes no change; in dry distillation, it evolves ammonia and arsenious acid, leaving a white, metallic, fusible residue of arseniuret.

The arsenious acid was determined by dissolving the salt in muriatic acid, diluting with water, and adding a standard solution of permanganate of potash; the silver was determined in the state of chloride, and the ammonia directly by M. Peligot's process. Analysis gave the following average numbers:—

Oxide of silver	58·3
Arsenious acid	25·2
Ammonia	16·7

which correspond with the formula $AsO^3, 2AgO + 4NH^3$, which requires oxide of silver, 58·2; arsenious acid, 24·8; and ammonia, 17·0.

Exposed to the air, this substance effloresces, loses its ammonia, and becomes yellow; at last it becomes black.

Arsenite of copper dissolves in ammonia with great readiness, giving an azure-blue fluid. When this solution, mixed with a little alcohol, is exposed to spontaneous evaporation, small blue crystals are deposited at the end of two or three days. These are oblique prisms, which undergo no change in the air, are insoluble in water, and contain copper, arsenic, ammonia and water. Dissolved in muriatic acid, this substance does not decolorize the permanganate of potash, and exhibits all the characters of the arseniates; it consequently no longer contains arsenious acid, but arsenic acid. Analysis gave numbers agreeing with the formula $AsO^5, 3CuO + 3NH^3 + 4HO$. It is therefore the ammoniacal arseniate of copper already obtained by M. Damour, but under circumstances in which this phænomenon of oxidation was not manifested.

When a solution of arsenite of ammonia is exposed to the air, the arsenic remains in the state of arsenious acid, and does not become oxidized at all; whilst in the present case the addition of a cupreous salt to the solution causes the oxidation of a corresponding quantity of arsenious acid. This is consequently oxidated at the expense of the air, and the action is due to the presence of copper; the arsenious acid acting first upon the binoxide of copper, so as to pass into arsenic acid, converting the oxide into protoxide. The latter, in presence of the oxygen of the air, becomes oxidated anew, forming arseniate of copper, which then combines with the ammonia.

If, instead of exposing the ammoniacal solution of arsenite of

copper to the open air, it be evaporated in the absence of air in an ammoniacal atmosphere, arseniate of copper is no longer formed, but a simple precipitate of Scheele's green.—*Comptes Rendus*, May 2, 1853, p. 793.

On some Organic Acids. By L. Chiozza.

Amongst the organic acids, on the nature of which we possess exact data, those with 2 atoms of oxygen are undoubtedly those of which the classification presents the least difficulty. Most of these acids, in fact, are homologous with formic acid, and the others are allied, by the same homological resemblances, either to benzoic or salicylic acid; amongst the latter are toluic, cuminic and anisic acids.

Besides these acids, there also exist some which only differ from those first mentioned by containing 2 atoms less hydrogen; their distinctive character consists in the facility with which oxidizing agents convert them into other acids of a less elevated order. Thus cinnamic acid, under the influence of nitric acid, gives benzoic acid; and coumaric acid, treated with potash in fusion, is converted into salicylic acid.

These facts have long been known to chemists, but no one has yet endeavoured to isolate the substance, the formation of which accompanies that of benzoic and cinnamic acids in these processes. This metamorphosis was only well known in the case of acrylic and oleic acids. It was known, in fact, that under the influence of hydrate of potash, the first of these acids is converted into acetic and formic, and the second into acetic and æthalic acids.

The experiments now to be detailed were undertaken in M. Gerhardt's laboratory, with the view of ascertaining whether cinnamic, coumaric, and angelic acids behaved in the same manner as those already mentioned in the presence of potash. Angelic acid being homologous in its composition with acrylic acid, there was reason to suppose that it would be equally so in its properties. Experiment confirms this view. If angelate of potash be heated with an excess of hydrate of potash, a very abundant disengagement of hydrogen is observed, and the residue no longer contains any trace of angelic acid; this acid is replaced by a mixture of acetic and propionic acids, which may be obtained from the saline mass by distillation with dilute sulphuric acid. The two volatile acids are then separated by the crystallization of their soda salts. In this manner considerable quantities of propionic acid, in a state of great purity, may readily be obtained. The analysis of the acetate and propionate of silver gave the numbers required by calculation.

This metamorphosis of angelic acid explains why, in preparing this acid according to Gerhardt's method, from essence of chamomile, very small quantities of angelic acid are often obtained, as an increase of a few degrees in the heat is sufficient to convert it into acetic and propionic acids.

By similar experiments, I ascertained that, by the action of pot-

ash, cinnamic acid is converted into benzoic and acetic acids, with evolution of hydrogen:—

$$\underset{\text{Cinnamic acid.}}{C^{7}H^{8}O^{2}} + 2HKO = \underset{\text{Acetate of potash.}}{C^{4}H^{3}KO^{2}} + \underset{\text{Benzoate of potash.}}{C^{7}H^{5}KO^{2}} + H^{2}.$$

Lastly, coumaric acid appears to behave in the same manner, although I have not succeeded in obtaining sufficient acetic acids in the products of the action of potash upon this substance to be able to prove its presence by analysis.

The action of potash upon acrylic, angelic, and oleic acids is explained by the following equations, which will also show the relations existing between them:—

$$\underset{\text{Acrylic acid.}}{C^{3}H^{4}O^{2}} + 2KHO = C^{3}H^{3}KO^{2} + \underset{\text{Formiate of potash.}}{C\ H\ KO^{2}} + H^{2}.$$

$$\underset{\text{Angelic acid.}}{C^{5}H^{8}O^{2}} + 2KHO = C^{2}H^{3}KO^{2} + \underset{\text{Propionate of potash.}}{C^{3}H^{5}KO^{2}} + H^{2}.$$

$$\underset{\text{Oleic acid.}}{C^{18}H^{34}O^{2}} + 2KHO = C^{2}H^{3}KO^{2} + \underset{\text{Æthalate of potash.}}{C^{16}H^{31}KO^{2}} + H^{2}.$$

Another acid is known, which from its composition may be considered as the fifth term of this series, namely, the damaluric acid, $C^{7}H^{12}O^{8}$, of Stædeler. If it be really homologous with the preceding acids, it would be converted by hydrate of potash into valerianic and acetic acids.—*Comptes Rendus*, April 18, 1853, p. 701.

On the Combinations of Boracic Acid with Oxide of Silver. *By* H. Rose.

The remarkable behaviour of boracic acid towards oxide of silver, which the author had long since partially investigated, was the real cause of his undertaking his comprehensive investigation of the influence of water in chemical decompositions. He had then found that a dilute solution of borax acted towards a solution of nitrate of silver in quite a different manner from a concentrated solution. From the latter, white borate of silver was obtained, which is completely soluble in much water; whilst by means of a dilute solution of borax, pure oxide of silver of a yellowish-brown colour is precipitated, and this is not dissolved by a large quantity of water. It was consequently perceived, that, in a dilute solution of borax, the action of the boracic acid is so entirely destroyed by the influence of the water, that the salt only acts upon nitrate of silver like pure alkali.

If concentrated solutions of equivalent proportions of neutral borate of soda ($NaO, BO^{3}, 8HO$) and nitrate of silver be mixed together in the cold, a caseous precipitate of a dingy yellow colour is produced. If this, after filtration, be not washed, but merely pressed between blotting-paper, it is found to consist almost entirely of neutral borate of silver ($AgO\ BO^{3}, HO$), only 1 atom of free oxide of silver being present for every 10 atoms of this compound; the precipitate derives its yellowish colour from the oxide of silver. But if the precipitate, after filtration, be washed with cold water, nearly all the boracic acid is extracted from the borate of silver.

The washing, however, on account of the solubility of the oxide of silver, cannot be continued so far that the wash-water no longer becomes turbid on the addition of muriatic acid. On examination, only 1 atom of boracic to 6 atoms of oxide of silver was found in the precipitate, which attracts carbonic acid from the air during drying.

If boiling concentrated solutions of the two salts be mixed together, a brown precipitate is immediately produced, which becomes darker in colour when the whole is kept boiling for some time. It consists only of oxide of silver. During drying, it attracts carbonic acid.

If concentrated solutions of equivalent proportions of biborate of soda and nitrate of silver be mixed whilst cold, a white precipitate is produced; but much borate of silver is dissolved in the filtered fluid. When the precipitate, after filtration, was pressed, without washing, between blotting-paper, it had, according to one analysis, the composition $3AgO, 4BO^3$. But it is not always of the same constitution, for some borate of silver obtained in the same manner, more recently examined by the author, had the composition AgO, BO^3. It had, however, been washed.

When cold concentrated solutions of the two salts are mixed together, and the resulting white precipitate washed with cold water, it acquires a strong brown colour on the surface, whilst internally it still remains white. When it had been washed so long that the wash-water no longer contained any nitric acid, it had essentially the composition $4AgO + 5BO^3$; it nevertheless contained some soda.

If boiling concentrated solutions of the two salts be mixed, the precipitate is at first white, but soon becomes of a dirty gray; when not washed, but merely pressed between blotting-paper after filtration, it has the composition $AgO\ BO^3, HO$. But if, after the mixture of the boiling solutions, the whole be heated to boiling, the gray precipitate becomes brown, and this colour becomes changed to a deep blackish-brown if the boiling be continued some time. If the compound be washed with hot water after filtration, the wash-water contains much borate of silver, and the residue consists of oxide of silver which has attracted carbonic acid during the washing. —*Bericht der Akad. der Wissensch. zu Berlin*, 1853, p. 43.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Cast Steel. By Dr. KARSTEN.

CHEMISTRY had already been established upon a scientific basis by the adoption of the doctrine of definite proportions at the time when attention was again directed to the compounds of iron with carbon. With regard to these substances, so important in the arts, the law of definite combining proportions did not appear to hold good; but the per-centage of carbon was greater in proportion as the carboniferous iron approximated more closely to steel, and from this to

cast iron. However, there still remained a possibility of reconciling this fact with the law, by assuming the existence of a definite carburet of iron capable of combining with iron in definite or indefinite proportions, and determining its characters. Still the existence of such a carburet of iron has never yet been proved. In the course of a former investigation of this subject, I was of opinion that I had really obtained such a substance. But the evidence of subsequent experience is entirely the other way; and even if such a compound were discovered, the difficulty would not be removed, for it would still be necessary to admit that it combined in indefinite proportions with iron. It would appear as if the combination of iron with carbon in indefinite proportions does not exceed a certain limit, and that the maximum per-centage of carbon is about 5·93.

The classification of the various kinds of carburetted iron, under the general names of cast iron, steel and bar iron, is entirely arbitrary, and based upon the physical characters. When entirely free from carbon, iron is so soft that it offers but little resistance to friction, and would be inapplicable to most of the purposes for which iron with more or less of carbon is employed. By combination with carbon within certain limits, it acquires greater hardness; the elasticity and ductility are increased. The increased hardness is especially remarkable when the strongly-heated metal is suddenly cooled. This character of some carburetted iron has been made the distinction between bar iron and steel, inasmuch as all bar iron which becomes harder when suddenly cooled is by universal consent termed steel. The analyses of a great number of varieties of iron has led to the result that the per-centage of carbon may rise to 0·2, or even 0·25, before the metal becomes considerably harder when suddenly cooled. The purer the iron is, the greater its freedom from adventitious substances, especially sulphur, silicium and phosphorus, the larger may be the per-centage of carbon requisite to determine its hardening when cooled suddenly. The best kinds of Swedish bar iron, and that made in Germany from spathic iron and brown iron ores, do not become very hard even when containing as much as 0·35 per cent. of carbon, although the hardness is such as to justify the appellation of steel-like iron. The transition from this kind of iron to true steel is so imperceptible, that it is necessary to adopt some arbitrary means of deciding whether the metal is bar iron or steel. If the carburetted iron acquires on sudden cooling such a degree of hardness as to give sparks when struck upon flint, it may be regarded as steel; and this degree of hardness requires a per-centage of carbon amounting for the less pure kinds of iron to 0·5, and for the nearly pure iron to 0·65. However, steel containing such a small per-centage of carbon is always but soft steel, which, to become capable of acquiring greater hardness, must be more highly carburetted. The hardness acquired upon sudden cooling increases as the per-centage of carbon increases, but not in the same proportion. For iron almost perfectly free from adventitious substances, a per-centage of 1·4 or 1·5 carbon corresponds with the highest capability of acquiring hardness and tenacity. With

a still higher per-centage of carbon, the steel acquires greater hardness; but its tenacity is lessened and the malleability decreases so rapidly with the increase of carbon, that with a per-centage of 1·75 it can scarcely be welded at all. When the per-centage of carbon amounts to 1·8, it is only with great difficulty that it can be forged, although with a very great degree of hardness it may still possess considerable tenacity. Steel which contains 1·9 per cent. and more of carbon can scarcely be forged at all, and with a per-centage of 2·0 the limit between steel and pig iron appears to be reached; for such metal in the soft state, that is, before being hardened, cannot be beaten out while hot without splitting and breaking under the hammer.

Steel, in virtue of the remarkable capability which it possesses, after cooling slowly from a high temperature, of being worked like soft iron, and then acquiring a considerable increase of hardness, without loss of tenacity on subsequent sudden cooling, has become a very valuable substance for various branches of industry. However, it has not yet been possible to refer the altered conditions of hardness presented by the slowly and suddenly cooled metal to any altered state of combination of the carbon and iron in steel. Such wide differences of hardness and softness as those presented by steel which has been submitted to these two modes of treatment, can only be regarded as resulting from a total alteration of its molecular structure. The conjecture that the state of combination of the iron and carbon in hardened and soft steel respectively must be very different, is rendered in a high degree probable from the circumstance that such a difference in the state of combination of the iron and carbon in the carburets with a larger per-centage of carbon—the different kinds of pig iron—may be proved to exist with perfect certainty. A distinction has always been made between white and gray pig iron. These substances differ so obviously in their characters—colour, hardness, tenacity and brittleness—that the fact could scarcely have been overlooked. In addition to this, the difference in their conditions of fusion must not be overlooked, the gray kind requiring a much higher temperature than the white iron, and passing almost suddenly from a solid to a liquid state, while the white iron not only fuses at a lower temperature, but before liquefaction becomes soft, and then pasty. Before a trustworthy method of separating carbon from iron had been discovered, it was supposed that this difference in the behaviour of white and gray kinds of iron was attributable to the per-centage of carbon, for on dissolving gray iron in acids a much larger quantity of carbon is left than when white iron is treated in the same manner. Now, however, it is known that this inference was erroneous, and that the characters of pig iron are dependent, not upon the greater or less per-centage of carbon, but upon the state of combination of the carbon and iron. The gray iron, when suddenly cooled after having been melted, is converted into white iron; and white iron, when exposed to a high temperature, after melting, and gradually cooled, is converted into gray iron, without the per-centage either of iron or carbon being in

any degree altered. Every kind of gray iron corresponds to a white iron with precisely the same per-centage of carbon; and the wholly different behaviour and characters of these two kinds of iron are no longer regarded as owing to the greater or less per-centage of carbon, since it is known that the gray soft iron, malleable at the ordinary temperature, is a mixture of steel or steel-like iron with carbon, while the white, hard, and brittle iron is a true chemical compound of iron with the entire quantity of carbon present.

The analogy between the gray and white pig iron on the one hand, and soft and hardened steel on the other, is unmistakeable; but no trace of uncombined carbon has ever been found in slowly cooled soft steel. Even cast steel, which contains from 1·9 to 2·0 per cent. of carbon, and which on account of this large per-centage can no longer be forged, has never been found to contain uncombined carbon after the slowest possible cooling. It is only when the per-centage of carbon amounts to 2·25 or 2·3, that carbon separates in the slowly cooled metal, and communicates to it the characters of true pig iron. If, therefore, a distinction is to be drawn between steel and pig iron, founded upon a character determined by the combining proportions, it would correspond with a per-centage of carbon amounting to 2·25 or 2·3, because a part of the carbon is then separated on gradually cooling the mass. The more the per-centage of carbon increases from this minimum to the maximum of 5·93, the lighter is the colour of the metal and the greater the hardness of the white variety. In the gray iron, on the contrary, the quantity of carbon which separates, and which determines the darker colour and greater softness of the metal, as well as the greater or less per-centage of carbon remaining in a state of chemical combination with the iron, is dependent upon the more or less gradual solidification of the melted mass. It is therefore not sufficient to know the per-centage of carbon in pig iron, as ascertained by analysis, in order to form an opinion as to the behaviour of the iron in question; but it is at the same time necessary to determine how much of that carbon is chemically combined with the iron, and how much is present only as a mere mechanical admixture. With regard to the metallurgical processes, the object of which is to separate the carbon from pig iron for the production of steel or bar iron, the state of combination in which the carbon exists is of far greater importance than the total per-centage of this element. White iron requires for this purpose methods and processes different from those applicable to gray iron; and cases may occur in which the smelter would be obliged to convert gray into white iron, even although this has to be effected by an addition of carbon, notwithstanding that its separation is the real object of his operations.

Although in the case of pig iron it is necessary to bring it into a liquid state, in order to convert the gray and soft variety into that which is white and hard, or, on the contrary, the former into the latter by rapid or slow cooling of the metal, in the case of iron with a smaller per-centage of carbon or steel, mere rapid or slow cooling, without any previous alteration of the state of aggregation, is sufficient

to convert the darker-coloured soft steel into the whiter hard steel, and the reverse. Judging from analogy, therefore, it is highly probable that changes in the state of combination of carbon and iron take place in the hardening and softening of steel, corresponding to the different states of combination of this element in gray and white iron, although these differences in the state of combination have not yet been proved by chemical evidence to exist in the case of steel as they have in raw iron. However, the hard and soft steels have never been regarded as special varieties, and there is no greater reason for regarding white and gray pig iron as special varieties, because the differences in colour, hardness, and tenacity are owing solely to the respective states of combination determined by conditions of tem perature, and not to any alteration in the combining proportions. If, however, gray and white iron are regarded as special varieties, in the same manner as graphite and diamond, it must not be forgotten that a perfectly analogous relation exists between hard and soft steels, which are not regarded as special varieties.

In the processes employed for decarbonizing pig iron and converting it into steel, it has not hitherto been possible to obtain a product of perfectly homogeneous nature. It is always necessary to sort the steel, in order to separate the harder parts containing more carbon from the softer, and these again from the steel-like iron. This absence of homogeneity in the product, resulting from the imperfection of the processes, led to an attempt to give the steel great uniformity of texture by melting. The so-called cast steel is really a much more homogeneous and trustworthy product than the raw steel, or that obtained by cementation, although its characters likewise depend upon the proper and careful selection of the material from which it is made. In consequence of the fact, that steel may be prepared by fusion, which, together with a large per-centage of carbon and consequent hardness, possesses homogeneity whatever may be the degree of hardness desired, cast steel has acquired such a well-merited reputation, that it is now always employed for articles in which great hardness is indispensable. However perfect the process for making cast steel may appear to be, it is still open to the disadvantage, that the selection of the suitable material must be entrusted to the judgement of the workman, and consequently that however homogeneous the product, the per-centage of carbon, the hardness and solidity of the steel cannot be determined with precision beforehand. Such imperfections in the practice of metallurgical operations are in every case unavoidable, when determinations of weight must be replaced by the practised eye of the workman. The per-centage of carbon in the material employed in making cast steel—cementation-steel—is different in every part of the section of the bars, so that the average per-centage of carbon in the charge of a crucible and the product of the casting cannot be determined with precision. Although the hardness of the English and good German cast steel corresponds tolerably well with that which is required, this result is solely attributable to the perfect acquaintance of the workmen with their materials, and their careful selection of it for this particular purpose. There would be no uncertainty as to the result,

if we possessed a material applicable to the preparation of cast steel in which the per-centage of carbon could be calculated. The white pig iron made from pure spathic and brown iron ores free from disseminated copper pyrites, and the per-centage of carbon in which may, without any considerable error, be assumed as 5·6*, is a material of this description. The per-centage of carbon in the best kinds of Swedish bar iron, and the iron which is made in Germany from pure spathic and brown iron ores, may very safely be assumed as 0·25 on the average. The above pig iron and this bar iron are the purest kinds known, containing only traces of silicium, from which likewise the cementation-steel used for making cast steel is never free. Both these kinds of iron are therefore of such a nature as to enable the operator to determine beforehand with precision the per-centage of carbon in a crucible-charge, and to produce cast steel of any desired degree of hardness by means of a simple calculation of the requisite proportion of the two kinds of raw material. If the per-centage of carbon in the melted product obtained in this way, and the characters dependent upon that per-centage, should be found to agree perfectly with calculation—a question to be determined only by experiments on a large scale—it might be expected that the production of cast steel from these materials would constitute a new phase of this branch of industry in Germany; for besides the trustworthiness of the operation, by which cast steel could be made of any desired degree of hardness and tenacity, it possesses œconomical advantages in the cheapness of the raw material. These advantages are for German industry of especial importance, from the circumstance that in many provinces of that country the pure white iron with lamellar facets is produced in large quantity, and not at all in other countries.

But the production of cast steel by melting together white iron and pure bar iron appeared to be liable to an objection far greater than that founded upon the impurity of the raw material, and this arose from the doubt as to whether the product of the fusion would be homogeneous. In my 'Handbuch der Eisenhüttenkunde' (3rd edition, vol. iv. p. 512), I have already expressed an opinion that this would not be the case, and have given the reasons which make it advisable to employ cementation-steel for making cast steel in preference to a mixture of pig iron and bar iron in suitable proportions. However, the question of practicability could only be decided by direct experiment; and it was, for the above-mentioned reasons, of sufficient importance to submit it to this test. Such experiments were made in the years 1846 and 1847, at the cast steel and file factory of M. Huth at Geitebrück near Hagen, and under the direction of the late superintendent Stengel, M. Huth having placed his factory at our disposal for the purpose.

The melting-crucibles employed were of such capacity, that from 30 to 35 lbs. could be melted at a time. The melted metal was as usual run off into cast iron moulds. The following is a brief statement of the results obtained in a great number of meltings, and the subsequent treatment of the cast steel:—

* Karsten and v. Dechen's Archiv für Mineralogie, vol. xxi. p. 501.

1. In the selection of the pig iron, it is of great importance to employ such as presents perfect lamellar structure, and not such as is partly fibrous or compact. The use of lamellar iron is necessary, not only in order that the per-centage of carbon in the charge may be calculated with accuracy, which cannot be done with fibrous or compact iron in which the per-centage of carbon varies greatly, but likewise and especially because the lamellar iron exercises the greatest solvent action upon the bar iron, so that even a comparatively much larger quantity of these kinds is but an imperfect substitute for the lamellar iron. Consequently good cast steel cannot be produced in this way without lamellar pig iron.

2. The extremely high temperature which bar iron requires for fusion appeared to render it necessary that it should be added to the charge in small fragments. On this account the first fusions were made with bar iron, which had been rolled into moderately thick sheets and then cut into pieces. However, it was subsequently ascertained that the solution of the bar iron in the liquid pig iron takes place without any difficulty, and that the product is equally good when thick pieces are used, so that finally masses of a cubic inch in dimensions were employed. By this means the expense of cutting the bar iron is obviated; at the same time the iron is less oxidized, and less room is taken up in the crucible, than when it is in small fragments.

3. In order to produce a homogeneous cast steel, the highest possible temperature is necessary for the fusion. Consequently very infusible crucibles, which are not liable to crack, are a much greater desideratum in the production of cast steel from pig and bar iron than even in the melting of steel itself. Of course the greater the number of meltings which can be made in one crucible, the greater is the œconomical advantage gained.

4. The melted metal must be run off into the cast-iron moulds as rapidly as possible, in order that the whole mass may cool uniformly. At the same time care must be taken that none of the slag is allowed to pass from the crucible into the moulds, for there is not time for the slag to separate from the metal; it solidifies in the midst of the steel, and renders the casting defective, and causes the bar to rend in rolling. This may be most advantageously obviated by taking the cover from the crucible while it is still in the furnace, and skimming off the slag with a ladle-shaped iron. The small quantity which then remains may easily be kept back in the ordinary way during the casting.

5. The cast steel, when allowed to cool *slowly* in the crucible, loses all coherence, and breaks down under the hammer or rollers. The cause of this appears to lie in the formation of carburets of iron, which do not remain combined with the rest of the steel containing less carbon.

6. The cast bars must, after they have cooled, be freed from all adhering granules of metal by means of a chisel. If this is neglected, the edges of the bars become broken in rolling.

7. In heating the cleaned bars for the purpose of further working, a bright red heat must be employed. This cannot be effected in a

satisfactory manner before a blast, because the temperature is not sufficiently uniform, and a uniform heat is indispensably necessary for the favourable result of the rolling or hammering. This can only be effected in a well-constructed reverberatory furnace, and most advantageously in one fed with gas, a slight excess of which is present.

8. It is preferable to roll the heated bars rather than to hammer them; but if a hammer is used, it must be of considerable weight.

9. The cast bars presented a perfectly homogeneous appearance, even after rolling. The bars were first rolled out square to a length of 4 feet, and then after reheating brought into the desired form. They admitted of being rolled into the thinnest sheets without cracking at the edges.

10. Even in making soft steel, for which purpose the crucible was charged with 25 lbs. of bar iron and 2 lbs. of pig iron, a perfect solution of the bar iron was effected by means of a strong heat. The product was a homogeneous steel, although, according to calculation, it could not contain more than 0·6 per cent. of carbon. The best, hardest, and most tenacious steel was obtained by fusing mixtures in which the calculated per-centage of carbon was 1·5 or 1·6. For this purpose the crucible was charged with 24 or 25 lbs. of bar iron and 8 lbs. of pig iron.

11. The cast steel, even that which is soft and in which the per-centage of carbon is only 0·6, differs essentially from the raw or melted steel in the circumstance that it cannot be welded without great difficulty. With a higher per-centage of carbon, it can only be welded under a coating of borax. With a per-centage of 1·25, it can no longer be welded at all. Although, on the one hand, this behaviour of the cast steel obtained in this way indicates its homogeneity, still it is a defect, one indeed which is likewise possessed by the English cast steel in a somewhat less degree.

12. The cast steel bears only low tempering heat, and acquires a very high degree of hardness, although at the cost of its tenacity. The proper mode of tempering it still remains to be ascertained.

13. The steel may be used for making the finest kinds of cutlery for files and chisels. For all purposes in which it is submitted to sudden and violent blows, it has proved destitute of the requisite tenacity. While very hard, it possesses considerable brittleness.

14. The last-mentioned character of the steel affords ground for doubting its certainly apparent homogeneity, and this conjecture is confirmed by the fact, that its tenacity and capability of being welded are considerably increased by remelting. If, however, it should prove to be impossible to produce a good cast steel in one melting, the œconomical advantages of this process would probably be altogether lost.

The further prosecution of these experiments has unfortunately been interrupted by the long illness and death of Superintendent Stengel, who had for a number of years afforded me valuable aid in carrying out a variety of experiments, which appeared to me to be necessary for the purpose of throwing some further light upon the metallurgy of iron.—Karsten and v. Dechen's *Archiv*, vol. xxv. p. 218.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Upon Palladamine. By Dr. HUGO MÜLLER.

PALLADIUM forms with ammonia a red and a yellow chlorine compound, which have hitherto been employed as characteristic means of distinguishing and separating this metal. Many chemists have already occupied themselves with the investigation of these substances; and the result of the most recent experiments upon them is, that, although so different in their external characters, they both contain the same elements in the same proportions.

The red compound was discovered by Vauquelin in 1814, and has since been more closely investigated by Kane, Fehling and Fischer. The yellow compound was discovered by Fischer, who found that the red substance was soluble in heated ammonia, but that those acids which saturate the excess of ammonia, throw down, instead of the red salt, a new yellow compound. Fehling has since found that the yellow substance which is produced when the red compound is heated to 392° F., either in the wet or dry state, is the same as that discovered by Fischer.

The author has been induced by Prof. Wöhler to institute further investigations upon this subject. He found that the yellow substance was dissolved plentifully by solution of caustic potash, forming a yellow fluid, without evolving any ammonia; this solution may even be heated to boiling without the ammonia being set free. The red salt behaves in the same manner, but first becomes converted into the yellow compound, and is only dissolved in this form.

This behaviour immediately calls to mind the remarkable newly-discovered basic substances, which contain platinum and the elements of ammonia in their composition, and are usually called the platinum bases. From the analogy between platinum and palladium, it might have been supposed with the greatest probability that this circumstance would be reproduced with the latter metal, and that the yellow compound might be the salt of such a palladium base. It is evident that the formula at which Fehling arrived, $PdCl + NH^3$, may also be written in the following manner:—

$$N\left\{\begin{matrix}Pd\\H\\H\\H\end{matrix}\right\}Cl$$ = chloride of palladammonium.

It is consequently the chlorine compound of an ammonium, in which the fourth equivalent of hydrogen is replaced by 1 equiv. of palladium. The red compound must be provisionally regarded as palladiochloride of ammonia = $PdCl + NH^3$.

This view has been completely confirmed by the experiments now to be described:—

Palladamine, $\left.\begin{matrix} Pd \\ H \\ H \\ H \end{matrix}\right\}$ NO.—Palladamine is produced when a solution of chloride, bromide or fluoride of palladium, or of sulphate or nitrate of protoxide of palladium, is precipitated with ammonia; the resulting precipitate again dissolved in an excess of ammonia, and then saturated with the corresponding acid. From the chloride and bromide the hydracids throw down the salts of palladimine as yellow crystalline precipitates, of which the chlorine compound above described forms the type; the sulphuric, nitric and fluoric acid salts, on the contrary, remain in solution, together with the ammonia salt which is formed at the same time; from this the pure salt cannot be separated.

The base may be isolated in two ways; either by stirring up the yellow chlorine compound with water, and mixing it with oxide of silver, or by decomposing the solution of the sulphate by hydrate of baryta.

In both cases an inodorous solution of a pale yellow colour is obtained; it has a strong alkaline reaction, and a harsh alkaline taste; when applied to the tongue, it produces insensibility of the part touched with it.

To obtain palladamine in the solid form, a high temperature must be avoided, and the access of air prevented during the evaporation. It is therefore best effected in a retort heated by the water-bath, or by placing the solution in shallow saucers under the air-pump over sulphuric acid.

At a considerable degree of concentration, a sediment gradually settles from the dark yellow solution; this goes on increasing until at length the entire fluid has dried up into this solid body. The mass thus obtained is distinctly crystalline under the microscope, and appears to consist of octahedra. If the evaporation has been carried on in a retort, or if it is hastened under the bell-glass by hot sand, the base is of a brown colour and of an amorphous resinous appearance.

If the action of air containing carbonic acid and of a too high temperature has been avoided, the palladamine obtained dissolves almost entirely in water; but a small residue always remains, and this, when acids are poured over it, evolves carbonic acid; with muriatic acid it forms muriate of palladamine and a yellow solution. This residue acts like a mixture of carbonate of palladamine with an oxide of palladium, and it is very probable that the presence of organic substances induces its formation. The solution filtered from this small residue behaves like that originally obtained.

Dry palladamine absorbs carbonic acid less readily, and remains unchanged in closed vessels.

Heated alone to a little over 212° F., no visible change is produced, but at a higher temperature it begins to glow at one point; and this extends rapidly through the entire mass, becoming sometimes so violent that the sample is projected.

It was impossible to prepare palladamine free from carbonic acid, and in a sufficiently pure state to be submitted to analysis; consequently a direct analysis could not be made. Nevertheless the circumstance that this base unites again completely with muriatic acid to form muriate of palladamine, is sufficient ground for the admission that the substance described is the palladamine of the formula above given.

Solution of palladamine throws down the bases from copper and silver salts; an excess of the precipitant does not redissolve the smallest trace of the precipitate, as would be the case if the smallest quantity of ammonia were present. If a solution of muriate of ammonia is added to a solution of palladamine, the yellow colour of the mixture disappears after some time; if it is heated, the odour of ammonia is distinctly perceptible; but if it is boiled, strong evolution of ammonia is produced, and the muriate of palladamine is formed, which remains in solution. If the boiling is continued until no more ammonia is evolved, yellow crystalline muriate of palladamine separates on the cooling of the solution. Sulphate of ammonia and other ammoniacal salts behave just like the muriate. From this remarkable reaction, it follows that palladamine is a stronger base than ammonia. If a solution of palladamine is exposed to the air in a shallow vessel only for a short time, it absorbs carbonic acid with such rapidity, that even after a few minutes' exposure acids produce an effervescence. This property also shows an essential difference from ammonia. A mixture of solution of alloxan and alloxantine, brought into contact with solution of palladamine, exhibits no murexide reaction, but reduces the palladium.

The watery solution of the base remains without change for a considerable time in contact with alcohol; the influence of light appears, however, to produce some change. But if the mixture is boiled, the palladamine is decomposed, with separation of metallic palladium.

When the solution of the base is heated by itself, no decomposition is perceptible even with gentle boiling; but if the boiling is continued and rendered more violent, the evolution of a slight odour of ammonia shows a decomposition, whilst at the same time a brown flocculent substance is separated. It is probable that the presence of minute traces of organic substances effects this decomposition; for from the strongly alkaline nature of this base, it is very probable that during filtration through paper organic particles may be dissolved. On the other hand, even long boiling does not destroy all the palladamine.

Carbonate of Palladamine.—Solution of palladamine attracts carbonic acid greedily from the air, and becomes changed into a cry-

stalline mass. This salt may also be prepared by double decomposition, by decomposing either the yellow chlorine compound with carbonate of silver or the sulphate with carbonate of baryta. In either case the salt of palladamine is stirred up with water; a slight excess of the carbonate is then added, and the mixture allowed to stand some time before filtration. The carbonate of palladamine is dissolved, and colours the supernatant fluid of a golden-yellow. Its preparation by means of carbonate of silver has the disadvantage, that a portion of the resulting carbonate of palladamine combines with the excess of carbonate of silver and the chloride of silver, and cannot be separated from them by water. As, however, the preparation of sulphate of palladamine also presents difficulties, the preparation of the carbonate from the chloride is always to be preferred. When the yellow solution obtained as above is evaporated by a gentle heat, beautiful golden-yellow octahedra, which may be recognised by the naked eye, are formed when the fluid has attained the necessary degree of concentration. These octahedra appear to belong to the isometric system, at least the eye can discover no irregularities. Sometimes the salt separates merely in segments of octahedra, which are remarkably large, but very thin, so that the salt appears in mica-like scales.

The solution of this salt, like that of the pure base, gives no murexide reaction. The dry salt readily dissolves in water, giving a strongly alkaline fluid, which throws down carbonic acid salts from the salts of lime, baryta, protoxide of mercury, silver, copper and protoxide of iron.

Sulphite of Palladamine, $N\left\{\begin{matrix}Pd\\H\\H\\H\end{matrix}\right\}O, SO^2$, is obtained when a watery solution of palladamine is saturated with sulphurous acid and evaporated at a gentle heat; or, in a more simple manner, from the yellow chloride, by bringing this into contact with a solution of sulphurous acid; the odour of the latter disappears after a short time, whilst the otherwise nearly insoluble chloride dissolves with a dark brownish-yellow colour. The chloride also, when moistened with water and exposed to a stream of sulphurous acid gas, becomes warm, and changes by degrees into a dark brown mass. The product obtained by the action of sulphurous acid dissolves in water; when brought to a proper degree of concentration, crystals of two kinds are deposited, which may readily be separated. The one salt forms dark orange-yellow octahedra; it is sulphite of palladamine; the other is greenish-yellow, and forms thin prismatic laminæ. It is the palladiochloride of ammonium discovered by Wollaston.

In order to separate the sulphite more readily from the mixture, alcohol may be added to the solution until a yellow precipitate is produced; if some more alcohol is then added, the greater portion of the palladium salt separates after some time. The solution of this salt must not be boiled with alcohol, as by this means the palladium is separated in metallic spangles.

Sulphite of palladamine dissolves readily in water; with stronger acids it evolves sulphurous acid. It unites very readily with ammonia, forming a very stable, colourless, crystalline salt, which belongs to the series of palladdiamine salts, which will be hereafter described.

In the pure dry state this salt is very stable. The presence of organic substances readily produces a reduction. Heated to a few degrees above 212° F., the salt remains without decomposition, but at a higher temperature it is decomposed rather violently.

Mixed with carbonate of soda and heated to redness, it gave 47·8 per cent. of metallic palladium. According to the above formula it should contain 48·3 per cent.

Sulphate of Palladamine, $N\left\{\begin{matrix}Pd\\H\\H\\H\end{matrix}\right\}O, SO^3$.—This, like the preceding compound, is obtained by saturating the pure base with sulphuric acid. It can also be prepared by the mutual decomposition of the chloride of palladamine and sulphate of silver. When a solution of the silver salt is poured over the yellow chloride in the cold, an action is soon visible, and the fluid acquires a yellow colour. The chloride of silver separated is also coloured yellow by some palladium, and still more so when higher temperatures are employed. The author has not investigated the cause of this circumstance more closely.

When a solution of sulphate of palladium is mixed with ammonia, a brown uncrystallized precipitate is produced, which is nearly completely redissolved in a great excess of the precipitant. This solution contains palladamine, but combined with ammonia forming palladdiamine united with sulphuric acid. If sulphuric acid is added to this solution, a yellow colour is produced, but no sulphate of palladamine is separated; and as this is mixed in the solution with sulphate of ammonia, it is impossible to separate sulphate of palladamine from it.

The salt crystallizes in small orange-yellow octahedra, which dissolve pretty readily in water. With muriate of ammonia and other chlorine compounds, this solution furnishes a precipitate of yellow chloride of palladamine.

The dry salt remains undecomposed and loses nothing in weight at 302° F.; but when heated to near 572° F., it changes suddenly, and becomes decomposed with great violence, leaving metallic palladium.

The analysis of the salt was effected by heating one portion to redness with carbonate of soda, to ascertain the quantity of palladium, and precipitating another portion with nitrate of baryta for the sulphuric acid. In this manner, 44·4 per cent. of palladium and 35·1 per cent. of sulphuric acid were found. According to the formula, the salt should contain 45·2 per cent. of palladium and 34·7 per cent. of sulphuric acid.

Nitrate of Palladamine.—By the mutual decomposition of the

yellow chloride of palladamine and nitrate of silver, a yellow solution is obtained, which behaves as nitrate of palladamine.

In the attempt to obtain this salt in a solid form, it becomes decomposed, as it appears to be exceedingly unstable. The residue obtained by the evaporation of the solution, when heated on platinum foil, is decomposed with great violence.

Iodide of Palladamine, $N\left\{\begin{matrix}Pd\\H\\H\\H\end{matrix}\right\}I$.—This compound has already been prepared by Fehling, and described by him as palladioiodide of ammonia.

Iodide of palladium dissolves readily with evolution of heat even in dilute ammonia, forming a pale yellow solution, which, when hydriodic acid or another acid is added to it, immediately acquires a dark colour, and deposits iodide of palladium as a reddish-yellow powder. When this is rapidly washed, quickly pressed between blotting-paper, and dried *in vacuo* over warm sand, it retains this original reddish-yellow colour; but if it remains longer in contact with moisture, it becomes, according to Fehling's observations, rapidly changed into a red mass of crystals, without any alteration in its composition. The same change is produced by boiling the reddish-yellow precipitate with water. If an unconcentrated solution of iodide of palladium in ammonia is allowed to stand a considerable time in a warm place, dark violet octahedra of iodide of palladium, with a semi-metallic lustre, gradually separate.

This salt is nearly insoluble in cold water, but rather more soluble in boiling water; if the solution is boiled for a considerable time, a trace of ammonia is evolved, and the fluid during evaporation deposits a reddish substance, which is apparently palladioiodide of ammonium. Boiling nitric acid dissolves the reddish-yellow compound with elimination of iodine, forming nitrate of palladium.

The composition of this salt, as ascertained by Fehling, is in perfect accordance with the formula above given.

Bromide of Palladamine, $N\left\{\begin{matrix}Pd\\H\\H\\H\end{matrix}\right\}Br$.—Ammonia added to a solution of bromide of palladium produces a red crystalline precipitate, which has the most striking resemblance to the chlorine compound produced under similar circumstances. Like the latter, this bromine compound also consists of minute, long, prismatic crystals, with rectangular terminal facets. This compound also passes over into a yellow salt under the same conditions as the red chlorine compound, and behaves generally so similarly, that it can only be distinguished from it by ascertaining the fact of its containing bromine.

If this compound is dissolved in heated ammonia, a nearly colourless fluid, sometimes of a faint yellow colour, is obtained; this, on the addition of hydrobromic acid, first becomes yellow, and then deposits a yellow crystalline substance. This crystalline pre-

cipitate is bromide of palladamine. Like the corresponding chlorine compound, it forms microscopic octahedra, grouped into arborescent and needle-like forms; it is insoluble in cold, but dissolves more readily in hot water. The solution, after long boiling, evolves some ammonia, and deposits a brown flocculent substance.

Boiled with muriatic acid, some hydrobromic acid is evolved; even long boiling, however, does not expel all the bromine, although the greater part of the salt is decomposed. The salt is readily soluble in acetic and sulphurous acids, in solutions of potash and soda, and of the alkaline carbonates.

If bromide of palladamine be boiled with nitric acid, some vapour of bromine is evolved, and on concentration, crystals of palladiobromide of ammonium are deposited; if the boiling be continued, this salt is also decomposed, and then dark violet octahedral crystals, with a metallic lustre, of palladioperbromide of ammonium are formed. Bromine and chlorine act like nitric acid. The salt contains 35·26 per cent. of palladium. Calculation gives 35·85 per cent.

Chloride of Palladamine.—This salt is nearly insoluble in water. If a large quantity of it is boiled with water, and the fluid then kept for some length of time at 61° F., the solution contains $\frac{1}{312}$th of the salt. If the boiling is continued a considerable time, replacing the water which is evaporated, the solution gradually acquires a dark yellow colour, evolves a slight odour of ammonia, and deposits a brown uncrystalline substance, which behaves like protoxide of palladium containing ammonia. If this brown solution is now allowed to cool, no chloride of palladamine separates, and crystals of palladiochloride of ammonium only appear when the fluid is further concentrated.

When the chloride is suspended in water, and chlorine gas passed into it, a brown colour appears even in a short time; slight evolution of gas takes place, and the salt is dissolved with a deep reddish-brown colour. If ammonia is then added, red palladiochloride of ammonia is precipitated. If the reddish-brown solution is boiled with solution of potash, ammonia is evolved. When the solution is concentrated, crystals of palladiochloride of ammonium are obtained. But if the introduction of chlorine gas is further continued, strong evolution of gas is produced, and the odour of chloride of nitrogen is perceptible; if the fluid is now allowed to cool a little, dark red, nearly black octahedral crystals of palladioperchloride of ammonium are separated.

Ammonia poured over these crystals is decomposed with great violence even in the cold, and palladiochloride of ammonia is formed. The continued action of chlorine gas destroys this salt, and perchloride of palladium remains in the solution.

Acids in general, when acting upon chloride of palladamine with the aid of a gentle heat, produce similar effects to those described as occurring in the formation of sulphite of palladamine. The corresponding salts of palladamine and palladiochloride of ammonium are formed.

The following equation will explain this process:—

$$2(H^3\,NPdCl)+SO^2+HO \text{ separate into } H^4\,NCl, PdCl$$

$$\text{and} \quad N\left\{\begin{matrix}Pd\\H^3\end{matrix}\right\}O, SO^2$$

$$2(H^3\,NPdCl)+SO^2+HO.$$

Sulphurous acid shows this action most perfectly, as it is a powerful solvent of the chloride even in the cold. As the action of the other acids must be assisted by heat, secondary products are generally formed.

Fluoride of Palladamine.—When chloride of palladamine is put into a solution of fluoride of silver, chloride of silver is instantaneously formed, and the supernatant fluid acquires a yellow colour. By gradual addition of the salt, all the silver may be thrown down as chloride. The yellow fluid obtained behaves in all respects like a solution of fluoride of palladamine; with muriatic acid or chlorides it gives yellow chloride of palladamine, and acts in the same way with hydrobromic and hydriodic acids.

An attempt to evaporate this solution, and prepare the salt in a solid form, gave no satisfactory result; for when the solution was heated in a platinum vessel to about 141°–159° F., it suddenly became turbid, evolved a slight odour of ammonia, and deposited a brown precipitate. This precipitate was similar to that which has already been repeatedly mentioned as resulting from the decomposition of the salts of palladamine; it contained however a small quantity of fluorine. The filtered fluid was colourless, with a somewhat ammoniacal smell; it contained much palladium and corroded glass; on this account all these investigations had to be carried on in platinum vessels. When this fluid had been a little evaporated, rather large colourless crystals were deposited from it on cooling; these were fluoride of palladdiamine.

Further attempts to prepare pure fluoride of palladamine in a dry form all failed, in consequence of the readiness with which the salt is decomposed. It is remarkable that it possesses this property in common with the oxysalts of palladamine; their great solubility also forms a remarkable deviation from the general character of the other haloid compounds.

With the fluoride the author concludes the description of the salts of palladamine, as the salts described sufficiently characterize the substance; palladdiamine and its compounds are next brought under consideration.

[To be continued.]

On the Coloration of the Salts of Protoxide of Manganese.
By A. Gorgeu.

I. *Purification of the Salts of Manganese.*

The cause of the coloration of the salts of protoxide of manganese has not yet been determined. They generally present a

faint rosy tint both in the crystallized state and in solution; but it is supposed that this colour is foreign to them, and that, when sufficiently purified, they are colourless. Chemists attribute this rose colour to the presence of a small quantity either of permanganic acid, or a salt of sesquioxide of manganese, or of a salt of cobalt; the most generally received opinion is, that it is due to both these latter causes.

From my own experiments on this subject, I think I may conclude that *these salts of manganese possess a rose colour independently of the three causes above mentioned.*

In the first place, I may observe that the presence of permanganic acid is inadmissible; it is sufficient to remember that the permanganates are decolorized by protosalts of manganese, with the production of an insoluble peroxide.

To establish the fact of the existence of a peculiar coloration in the salts of protoxide of manganese, it is only necessary to show that they may be obtained of a rose colour after the sesquioxide and the cobalt have been entirely removed.

I will commence by proving that the sesquioxide is not an essential cause of coloration. I have ascertained that solutions of salts of the sesquioxide are instantaneously reduced by sulphurous acid, sulphuretted hydrogen and sulphuret of manganese. Now, after the addition of these reagents, the solution retains its slight coloration; this can therefore be attributed to no extraneous cause except the presence of cobalt.

The crystallized commercial salts of manganese, particularly the sulphate, are those which I have employed in my investigations; they may contain small quantities of copper, iron, cobalt and nickel.

The process on which I have depended for the purification of the solutions of these salts rests upon a reaction of the sulphuret of manganese, which completely precipitates these four metals from their solutions. A fluid containing only $\frac{1}{200,000}$dth of one of them communicated a very distinct brown colour to a considerable quantity of the sulphuret on ebullition.

The purification of the salts of protoxide of manganese may be performed either in the cold or with the assistance of heat; in the cold, by shaking the impure solution for about a quarter of an hour with a sufficient quantity of the sulphuret, after saturating the mixture with sulphuretted hydrogen; by heat, by keeping the mixture at the boiling-point for a few minutes, without the addition of sulphuretted hydrogen.

For purifying the sulphate of manganese, I have employed in preference pure sulphuret of barium saturated with sulphuretted hydrogen; this presents the double advantage of not diluting the solution, and of saturating it with sulphuretted hydrogen at the actual moment of precipitation. The addition of a sufficient quantity of the reagent may be known, when the filtered liquid furnishes, on the addition of more sulphuret, a precipitate of a pure flesh colour.

Having treated solutions of sulphate, nitrate, muriate, and acetate

of manganese in this manner, I have ascertained that the filtered liquids are always rose-coloured, and that their tint is not weakened by the prolonged action of sulphurous acid, or a fresh purification with sulphuret of barium, or boiling for half an hour with sulphuret of manganese, or by standing twenty days in the cold in contact with the latter reagent.

Solutions of salts of the protoxide of manganese consequently preserve their rose colour, however we may repeat or prolong the action of the sulphuret. If we admit that this tint is due to some extraneous cause, as the salts of the sesquioxide of manganese are decomposed by the reagents employed in the purification, it must necessarily be attributed under these circumstances to a small quantity of cobalt, the action of the sulphuret upon which is prevented by the salt of manganese. I have therefore to prove that there is no cobalt in the liquid.

For this purpose I admit, in fact, that the cause of this colour may be a certain quantity of cobalt which has escaped the action of the sulphuret. If the quantity of this be estimated by comparing together the tints of solutions of manganese and cobalt, it appears that a solution of sulphate of manganese containing half its weight of the salt, presents, after being completely purified, a rosy tint distinctly of the same intensity as that of a solution of chloride of cobalt ($CoCl, 6HO$) containing 0·26 per cent. of the salt. In such a solution the proportion of cobalt to the manganese is $\frac{4}{1000}$. Sulphuret of barium added to this solution gives a precipitate of a very pure flesh colour.

If, before adding the reagent, a quantity of cobalt equal only to the one hundred and fiftieth part of the quantity the liquid is supposed to contain, or in other words $\frac{1}{40,000}$dth of the weight of the manganese, be added, a blackish precipitate is immediately obtained in the cold. The results would certainly be the same in operating upon the chloride and nitrate of manganese. Now if the liquid already contains a certain quantity of cobalt, how is it that a quantity one hundred and fifty times less communicates a tint so different to the sulphuret of manganese? Can it be supposed that there exist definite combinations between the salts of manganese and those of cobalt, in which the relation between the two metals is always $\frac{4}{1000}$dths within a forty-thousandth part?

I believe therefore that I have proved that the three supposed causes of the coloration of the salts of protoxide of manganese are insufficient to account for this coloration in all cases; and it would result from this investigation, that *concentrated solutions of these salts are of a rose colour.*—*Comptes Rendus*, May 16, 1853, p. 861.

Formation of almost pure Protoxide of Nitrogen by the Action of Nitric Acid on Sal-ammoniac. *By* J. Lawrence Smith.

The experiments made with nitric acid heated with sal-ammoniac, to test the character of the decomposition, have resulted in the discovery of a new method for procuring protoxide of nitrogen with the aid of a very low temperature. Among the experiments

the following were quantitative. 2 grms. of sal-ammoniac were placed in a glass flask, and ½ an oz. of nitric acid poured upon it; the flask was connected with a small wash-bottle containing a little water, and from this latter a tube passed into a pneumatic trough filled with hot water; heat was applied to the flask, and before the temperature reached 140° F., a gas began to be given off, and at 160° it came off rapidly, and continued to do so after the lamp was withdrawn. A small amount of red fumes appeared in the flask, and were condensed in the wash-bottle; the gas that passed over was collected in a receiver, and measured 1008 cub. centims.; the gas smelt of chlorine; the flame of a candle burnt with an increased brilliancy when introduced in it; the candle was re-ignited when extinguished, if a burning coal remained on the end of the wick; no red fumes were formed when it came in contact with the air, and the gas was absorbable by cold water. The properties were those of protoxide of nitrogen. In another experiment the gases were collected at different stages of the process in phials over hot distilled water, and a solution of caustic potash introduced, and shaken up for some time; this latter was subsequently analysed for the chlorine it absorbed, and in three different portions, collected at the beginning, middle and end of the process; the proportions of the chlorine to the whole bulk of the gas were $\frac{1}{37}$, $\frac{1}{29}$ and $\frac{1}{16}$. The amount of protoxide of nitrogen due to the ammonia in 2 grms. of sal-ammoniac and its equivalent of nitric acid is 887 cub. centims. The gas freed from chlorine, on being shaken up with cold water for some time, was found to be almost entirely absorbed by the water. What remained was a mixture of nitrogen and a little air; some nitrous or hyponitrous acid forms during the whole process if concentrated nitric acid be used; if however it be diluted, little or none is formed, and the gas is readily given off at about 212° F.

In all my experiments, the protoxide of nitrogen constituted from $\frac{7}{8}$ths to $\frac{24}{25}$ths of the gaseous products; and when washed from its chlorine by a little lime-water or soda, possessed all the properties of pure protoxide of nitrogen; and I would recommend it as a convenient way of forming this gas, especially when not required for respiration.

The character of the decomposition which takes place is somewhat curious and unexpected. At first I supposed that the decomposition consisted in the formation of equal volumes of NO, Cl and N; but it appears that such is not the case, and that all but a very small portion of the ammonia with its equivalent of nitric acid is converted into NO, the liberated hydrochloric acid mixing with the excess of nitric acid; a little of the sal-ammoniac and nitric acid does undergo the decomposition first supposed, and in this way only can the small amounts of chlorine and nitrogen be accounted for. At the time this method was first tried, I also tried the decomposing effects of nitrate of ammonia on sal-ammoniac, that has been shown by Mauméné (Comptes Rendus, Oct. 15, 1851) to result in the formation of chlorine and nitrogen; but the difficulty of controlling the decomposition once commenced, the puffing up of the mixture,

and the necessity of having the salts dry to begin with, render this method (which was proposed by the author for forming chlorine) useless in processes for removing the sal-ammoniac in analysis.—Silliman's *Journal*, March 1853.

On the Insolubility of Native Realgar (AsS^2) *in Carbonate of Ammonia.* *By* C. Greville Williams.

It is usual in works on qualitative analysis to give, as a distinction between the sulphurets of arsenic and antimony, the difference of solubility in carbonate of ammonia; the former being readily, the latter scarcely, if at all, soluble in that reagent.

A remarkably beautiful and pure specimen of native realgar, although in extremely fine powder, was found to be absolutely insoluble in a strong solution of carbonate of ammonia. It was therefore dissolved in nitromuriatic acid, the solution neutralized, sulphide of ammonium added in excess, and the solution filtered from a trace of sulphide of iron; the addition of hydrochloric acid to the filtrate gave a rich lemon-yellow precipitate, easily soluble in carbonate of ammonia, which gave all the characteristic reactions of arsenic.

It is important that this property of native realgar should be borne in mind in the qualitative examination of arsenical minerals.

ANALYTICAL CHEMISTRY.

On the Quantitative Determination of the Alkalies in the Siliceous Minerals not soluble in Acids. *By* J. Lawrence Smith, M.D., Professor of Chemistry in the University of Virginia.

1. In the examination for alkalies in the class of minerals alluded to in this article, it is usual to devote a separate portion of the mineral to their special determination, without having reference to any of the other ingredients contained in the mineral. This method of proceeding naturally recommends itself; because a fusion with carbonate of soda is so greatly superior for the determination of all other ingredients, that even the attempt to control the result of the soda fusion by making use of the one for the alkalies, to arrive at the other substances as well as the alkalies, will in many instances embarrass the analyst as to his results.

2. It is only in cases of absolute necessity that one portion of the mineral should be used to estimate all its constituents; and this condition of things will be alluded to in another part of this paper, as reference is now had to the quantitative determination of the alkalies, discarding whatever else the mineral may contain.

3. In the determination of the alkalies in silicates not soluble in acids, three important points present themselves:—

I. The means necessary to render the silicate soluble.

II. The separation of the other ingredients from the alkalies, more especially magnesia.

III. The removal of the sal-ammoniac unavoidably accumulated in the process of analysis.

In all three of these, the processes adopted will be found to differ essentially from those now in use; and they are made known only after much experience by the author, in which their advantages have been most fairly tested, comparatively with methods already employed. In order that these processes may serve equally well in the hands of others, they will be given with some detail.

I. *Method of rendering the Silicate soluble.*

4. To render the silicate soluble, various plans have been proposed, all of which have their objections. Among the agents used for the purpose are baryta and several of its compounds, viz. the nitrate, carbonate and chloride.

5. The first of these is undoubtedly the best decomposing agent of the four, could we use a platinum crucible to heat the mixture of it and the mineral; as it is, a silver crucible is necessary, and this is not always capable of standing the requisite heat. According to Rose, "the silver crucible must be very strong, for if thin, the action of a red heat might crack it, and a portion of the fused mass would ooze out through the crevices." It also may happen that a heat higher than the point of fusion of silver is necessary to a complete decomposition of the mineral.

6. All that is here said of caustic baryta is equally applicable to nitrate of baryta.

7. The chloride of barium has been lately proposed; but its decomposing properties are very feeble, as the chlorine in combination with the barium is not liberated at a white heat, and few silicates are able to produce the decomposition. It may succeed with some of the felspars, but decomposes very imperfectly even the micas. So it is rather a risk to employ it with an unknown substance.

8. The carbonate of baryta is the compound of baryta most generally employed for silica decompositions; still this is attended with much difficulty, owing to the infusibility of this salt, and the impossibility of driving off the carbonic acid by heat alone; and even if this latter were possible, the objection pertaining to caustic baryta would then arise.

9. The following extract from Rose's 'Analytical Chemistry' (translation by Normandy, in a note by the translator) presents fairly the difficulties attending this method of decomposing the silicates:—

"The heat applied is so intense, that some precautions must be taken. The platinum crucible containing the mixture should be exposed first to the heat of an argand lamp, and when the mass begins to agglutinate, the crucible should be closed, and its cover tied down with platinum wire, then placed in a Hessian crucible, closed up also; the whole is placed upon an inverted crucible, and submitted to the action of the blast of a wind-furnace, beginning first gradually with a red heat, piling on more coke, so as to fill up the furnace, and increasing the heat to the highest possible pitch, until

the Hessian crucible begins to soften. It is absolutely necessary to the success of the operation that the Hessian crucible should be closed as well as possible, which is best done by luting the cover with fire-clay; the Hessian crucible and its cover having fused together, cannot be separated, except by breaking," &c. &c.

It will be seen, in reading this extract, that the heat required is not ordinarily at the command of most chemists; in fact no other variety of furnace than a Sefstroem can be depended on for a complete decomposition.

10. Caustic lime and its salts have also been recommended and long used for the more imperfect decomposition of silicates, as for obtaining lithia from spodumene and lepidolite. Lime or its carbonate, well mixed with many silicates finely pulverized, will decompose them completely at a white heat; but no one salt of lime is capable of meeting the demand of the entire range of alkaline silicates.

11. In consideration of these difficulties, Berzelius proposed the use of hydrofluoric acid; and this method, when applied with the numerous precautions required, will serve to decompose almost all silicates; still, according to Rose, there are siliceous compounds that cannot be completely decomposed by hydrofluoric acid. Besides, this acid is a most disagreeable one to manipulate with, whether we employ Brunner's apparatus or Laurent's method, or, what is always the best, the *concentrated acid* previously prepared. I may also add, that the necessity of using sulphuric acid, after the decomposition is made, is another objectionable feature in this process.

12. The above furnishes a hasty review of the methods we are now possessed of for decomposing the silicates, in order to determine their alkalies; their merits can be contrasted with those of the method about to be described.

13. The decomposing agent which I present as a substitute for all others, and as capable of meeting the demands proposed in the commencement of this article, is *a mixture of carbonate of lime and fluor spar.*

14. Carbonate of lime I have used for more than six years for decomposing certain of the alkaline silicates, and more successfully than carbonate of baryta; still, in numerous instances, the decomposition was far from complete and the method unsatisfactory. Notwithstanding these failures, I felt convinced that lime was the most powerful decomposing agent that could be conveniently employed for this purpose, as it could be used in its caustic state in a platinum crucible without injuring the latter, although exposed to the highest temperature: when its carbonate is used, a red heat sufficed to drive off the carbonic acid and bring the mineral under the action of caustic lime, a circumstance that does not take place with carbonate of baryta; and it is well that it does not, for otherwise the platinum crucible would be seriously injured.

15. It was evident that the only obstacle in the way of lime decomposing the silicates as thoroughly as caustic potash, was the impossibility of fusing the mixture, and thereby bringing the pul-

verized mineral and lime intimately in contact. This difficulty overcome, I felt confident of success. Without detailing the various methods resorted to, it will suffice to state that the object in view was to use some flux along with the mixture of the silicate and lime, which would render the mixture fluid at a bright red heat. The two substances which recommend themselves, after many experiments, are the fluoride and chloride of calcium, neither of which have any marked decomposing action on the silicates; in fact, their action is simply that of fluxes, which enable the lime and silicate to come in contact in a liquid state, effecting nothing beyond that. It is with the *fluoride of calcium* that we have to do in this part of the paper, leaving the details on the use of the chloride of calcium until further experiments are made to test fairly its value.

16. The manner in which I proceed is as follows:—

Pulverize the silicate to a sufficient degree of fineness; it is not required that the lævigation be carried to any great extent; mix intimately, in a glazed porcelain mortar, a weighed portion of the mineral with 1 part of pure fluor spar and 4 to 5 parts of precipitated carbonate of lime*, and introduce it into a platinum crucible capable of holding three times the bulk of mixed powder. The platinum crucible should then be placed in one of earthenware, with a little magnesia on the bottom. [I always prefer the crucible made in France, called Beaufay's crucible, to enclose platinum crucibles when heated in a furnace, as their form and cleanliness make them superior to the Hessian crucible for this purpose.] The crucible may then be covered, and introduced in any form of furnace where a bright red heat can be procured.

17. I have been using a common open portable furnace, heaping charcoal over the top of the crucible; and so easily does the effect take place, that in no instance has there been a failure of complete decomposition with as simple a means of heating as the above; and I have ascertained that an alcoholic lamp, with a large circular wick, such as Jackson's lamp, urged with a bellows, will answer for making a complete decomposition of zircon in twenty-five minutes. This circumstance is not stated to recommend the use of a lamp for every mineral decomposition, when a simple portable furnace and charcoal are so accessible, and their effects so much more to be depended upon than a lamp. From thirty minutes to one hour's exposure to the heat is recommended.

* The fluor spar used is the transparent variety, free from all impurities; it is easily and abundantly procured in this as well as in all other countries. The carbonate of lime is made by dissolving calc spar or pure marble in hydrochloric acid (the common acid may be used), adding an excess of the carbonate; lime-water or milk of lime is then poured on the solution until it is alkaline. By this means any oxide of iron, alumina, or magnesia will be thrown down. To the filtered solution, a solution of carbonate of ammonia is added, and the precipitate washed several times with distilled water. It is best to prepare one's own carbonate of lime, for as a general rule little reliance can be placed on the carbonates of lime, baryta, strontia, &c. sold as being precipitated by carbonate of ammonia, for in more than one instance I have found the carbonate of baryta sold as a carbonate of ammonia precipitate to contain soda.

18. It was an important point to test first how far this mixture could decompose the silicates without distinction as to their containing alkalies; for it was a very simple conclusion, that if those silicates most difficult of decomposition, and containing no alkalies, were completely decomposed by this process, all others must naturally give way under its action. The silicates experimented on were *zircon, kyanite, beryl, topaz, spodumene, margarite, margarodite,* and *felspars of different descriptions.* All were readily decomposed by the method just described, and without any particular care in lævigating them; 1 grm. of the zircon, for instance, after being crushed in the diamond mortar, was rubbed up for fifteen minutes in a large agate mortar, and used. Its complete decomposition was not only shown by its solution in hydrochloric acid, but by the amount of zirconia obtained, which was 64·8 per cent. with little iron. This concludes the first point to be considered in this article, namely, the means necessary to render the silicates soluble; the next point is the separation of the alkalies.

II. *Separation of the other Ingredients from the Alkalies.*

19. The platinum crucible with its fused contents is laid on its side in a capsule of platinum or porcelain; the latter can be used with perfect safety to the accuracy of the result. A quantity of dilute hydrochloric acid is poured into the capsule, 1 part of acid to 2 of water; the whole is heated over a lamp, when the contents of the crucible are rapidly dissolved out; the crucible is taken out and washed over the capsule; the contents of the capsule are then evaporated to dryness over a sand-bath, and if thought necessary, it may be completed over the lamp, without danger of the spitting which occurs in the soda fusion; this evaporation to dryness is not absolutely necessary, but the advantage of it is, that any great excess of hydrochloric acid is got rid of, and the precipitate in the next operation is less bulky than it otherwise would be.

20. To the dry mass a little hydrochloric acid is added, and then 3 or 4 oz. of water, or more, as the occasion may require; it is then boiled for a short time in the same capsule, allowed to cool down a little, and then a concentrated solution of carbonate of ammonia is slowly added until there is an excess of the same; the solution becomes at first quite thick with the precipitate, but in a short time (especially with a little warming over the lamp) the precipitate accumulates in a more or less granular state, and afterwards occupies less space in the filter than the alumina it might contain (in a felspar, for instance), were this latter precipitated separately by ammonia; and this circumstance is of much importance in diminishing the length of the operations and the amount of water accumulated by filtering it from several precipitates.

21. It will be seen that thus far the operations have been carried on in the capsule in which the fusion was dissolved. The contents of the capsule are now thrown on a filter, but before doing this it is well to pour on a little of the solution of the carbonate of ammonia, and see if the clear part of the liquid be rendered turbid, in

other words, ascertain if sufficient carbonate of ammonia had been originally added.

22. The solution that passes through the filter contains much sal-ammoniac, the alkalies of the mineral and a little lime. If magnesia be one of the ingredients of the silicate examined, some of this is also present, and in still rarer instances some of the earths soluble in carbonate of ammonia. This last complicates in no degree the remaining steps in the analysis. It is best to let the filtrate pass into a glass flask; the washings of the filter are collected in another vessel, and concentrated to a small bulk, added to the first filtrate, and the whole boiled for some time to drive off the carbonate of ammonia*. When no great haste is required in the matter, the whole filtrate (first portions as well as the washings) are collected in a beaker, and concentrated over a sand-bath. What remains now to do is to separate from the alkalies the substances above alluded to. I commence by getting rid of the sal-ammoniac; and this brings me to the third part of this paper.

III. *The removal of the Sal-ammoniac unavoidably accumulated in the Process of Analysis.*

23. This is probably one of the greatest annoyances to the analyst in his examination of minerals,—1st, from the manner in which the salt creeps up the sides of the vessel in which the evaporation to dryness is carried on; and 2ndly, from the great difficulty of preventing loss of the chlorides of the fixed alkalies during the volatilization of the sal-ammoniac. A better idea is formed of this by an experiment with a known quantity of the alkalies mixed with sal-ammoniac. An array of the precautions requisite to be taken can be seen in Rose's last edition (German), pages 6 and 7. Owing to these difficulties, which my experience has often led me to contend with, the method about to be mentioned was contrived. It recommends itself both on account of its simplicity and certainty of operation.

24. Having some time back noticed the decomposing effect produced by heating sal-ammoniac with nitric acid, the nature of the decomposition was investigated, to see how far it could be made use of to decompose entirely the sal-ammoniac; the result of the investigation was, that the sal-ammoniac could be completely decomposed at a low temperature into gaseous products, and it was immediately adopted in my analytical process with the greatest satisfaction, both as to accuracy of results as well as œconomy of labour†.

25. The manner of proceeding is as follows:—To the filtrate and washings concentrated in the way mentioned (22), and still remaining in the flask, pure nitric acid is added, about 3 grms. of it to every gramme of sal-ammoniac supposed to exist in the liquid; a little habit will suffice to guide one in adding the nitric acid, as even a large excess has no effect on the accuracy of the analysis.

* What remains in the filter is silica, alumina, fluoride of calcium, oxide of iron, carbonate of lime, &c.

† See page 250.

26. The flask is now warmed very gently; and before it reaches the boiling-point of water, a gaseous decomposition will take place with great rapidity. This is caused by the decomposition of the sal-ammoniac in the manner described at p. 250. It is no advantage to push the decomposition with too great rapidity; a moderately warm place on the sand-bath is best adapted for this purpose. With proper precautions, the heat can be continued, and the contents of the flask evaporated to dryness in that vessel; but it is more judicious to pour the contents of the flask, after the liquid has been reduced to $\frac{1}{2}$ an oz., into a porcelain capsule (always preferring the Berlin porcelain) of about $3\frac{1}{2}$ to 4 inches diameter, inverting a clean funnel of smaller diameter over it, and evaporating to dryness on the sand-bath or over a lamp. I prefer the latter, as at the end of the operation the heat can be increased to 400° or 500°.

27. By this operation, which requires no superintendence, 100 grms. of sal-ammoniac might be separated as easily and safely as 1 grm. from 5 milligrms. of alkalies, and no loss of the latter be experienced. What remains in the capsule occupies a very small bulk; this is now dissolved in the capsule with a little water (the funnel must be washed with a little water), small quantities of a solution of carbonate of ammonia added, and the solution gently evaporated nearly to dryness. This is done to separate what little lime may have escaped the first action of the carbonate of ammonia, or may have passed through the filter (22) in solution in carbonic acid. If any of the earths soluble in carbonate of ammonia existed in the mineral, those now become separated along with the lime.

28. A little more water is now added to the contents of the capsule, and the whole thrown on a small filter; the filtrate as well as washings are received in a small porcelain capsule. The liquid contains only the alkalies (as chlorides and nitrates) mixed with a minute quantity of sal-ammoniac. This is evaporated to dryness over a water-bath, and then heated cautiously over the lamp to drive off what sal-ammoniac may have formed (27), which is exceedingly minute if the process as pointed out be closely adhered to. It is not absolutely necessary to heat the capsule over the lamp, to get rid of the sal-ammoniac, for the little sulphate of ammonia which may be formed in the next step is easily removed in the final heating in a platinum vessel.

29. On the contents of the capsule, as taken either from the water-bath or as after being heated over the lamp, pure dilute sulphuric acid is poured (1 part acid, 2 water), and the contents boiled for a little time, when all the nitric acid and chlorine in combination with the alkalies will be expelled; the acid solution of the alkalies is now poured into a platinum capsule or crucible, evaporated to dryness, and ignited. In order to ensure complete reduction of the bisulphates into the neutral sulphates, the usual method must be adopted of throwing some pulverized carbonate of ammonia into the platinum capsule or crucible, and covering it up so as to have an ammoniacal atmosphere around the salt, which will ensure the volatilization of the last traces of free sulphuric acid. The alkalies are

now in the state of pure sulphates, and may be weighed as such. The manner of separating the alkalies from each other will be mentioned in the second part of this paper.

30. Thus far the mineral has been supposed to contain no magnesia. If this alkaline earth be present, we take the residue as found in the capsule (26), dissolve it in a little water, then add sufficient pure lime-water* to render the solution alkaline; boil and filter; the magnesia will in this simple way be separated from the alkalies. The solution which has passed through the filter is treated with carbonate of ammonia in the manner alluded to (27), and the process continued and completed as described (28, 29).

In the second part of this paper, qualitative examinations of the alkalies in silicates will be alluded to, as well as the separation of the alkalies from each other.

Summary.—Fuse 1 part of mineral with 1 of fluoride of calcium and 4 to 5 of carbonate of lime; dissolve out the contents of the crucible with hydrochloric acid; evaporate to dryness, and redissolve; precipitate with carbonate of ammonia; filter, boil, and concentrate the filtrate; add nitric acid, heat, and evaporate to dryness; dissolve the dry mass in a little water, and treat with carbonate of ammonia; filter and concentrate, then add sulphuric acid, boil for a little while, pour in a platinum crucible, evaporate to dryness and ignite. If magnesia be present, treat with lime-water prior to the last application of carbonate of ammonia.—Silliman's *Journal*, March 1853.

On the Analysis of Copper and Zinc Alloys. *By* H. Spirgatis.

It has been stated by Rivot and Bouquet, that the separation of copper and zinc by means of sulphuretted hydrogen is imperfect; and as a great number of analyses have been made by this method, the author has instituted a number of experiments upon it.

He finds that when sulphuretted hydrogen is passed through a solution of copper and zinc containing but a moderate quantity of free acid, sulphuret of zinc is precipitated together with sulphuret of copper.

In the author's experiments, the metals were oxidized by nitric acid, and the hydrochloric acid solution treated with sulphuretted hydrogen. The zinc was then precipitated by carbonate of soda, and weighed as ignited oxide.

In the experiments 1 to 5 the quantity of free acid in the solution was small.

1. A mixture of $\left\{\begin{array}{l}\text{zinc} = 0{\cdot}656 \text{ grm.} \\ \text{copper} = 0{\cdot}720 \text{ grm.}\end{array}\right\}$ gave 0·786 grm. of oxide of zinc not precipitated by sulphuretted hydrogen, equivalent to 0·631 grm. zinc. Consequently 3·81 per cent. were precipitated with the copper.

* If lime-water is made, it is well to make it of lime of the best quality, and the first two or three portions of distilled water shaken up should be thrown away, as containing the small amount of alkalies sometimes present in lime.

2. A mixture of $\left\{\begin{array}{l}\text{zinc} = 0{\cdot}612 \text{ grm.}\\ \text{copper} = 0{\cdot}852 \text{ grm.}\end{array}\right\}$ gave 0·754 grm. of oxide of zinc not precipitated by sulphuretted hydrogen, equivalent to 0·605 grm. zinc. Consequently 1·1 per cent. was precipitated with the copper.

3. A mixture of $\left\{\begin{array}{l}\text{zinc} = 0{\cdot}721 \text{ grm.}\\ \text{copper} = 0{\cdot}602 \text{ grm.}\end{array}\right\}$ gave in the same way 0·882 grm. oxide of zinc = 0·708 zinc. 1·8 per cent. was precipitated with the copper.

4. A mixture of $\left\{\begin{array}{l}\text{zinc} = 1{\cdot}328 \text{ grm.}\\ \text{copper} = 0{\cdot}660 \text{ grm.}\end{array}\right\}$ gave 1·554 grm. of oxide of zinc = 1·247 zinc. 6·09 per cent. were precipitated with the copper.

5. A mixture of $\left\{\begin{array}{l}\text{zinc} = 0{\cdot}876 \text{ grm.}\\ \text{copper} = 0{\cdot}931 \text{ grm.}\end{array}\right\}$ gave 0·902 grm. of oxide of zinc = 0·724 zinc. 17·34 per cent. were precipitated with the copper.

When, on the contrary, very acid solutions are employed, the separation of these metals may be effected by sulphuretted hydrogen with the greatest accuracy; thus—

6. A mixture of $\left\{\begin{array}{l}\text{zinc} = 0{\cdot}768 \text{ grm.}\\ \text{copper} = 0{\cdot}825 \text{ grm.}\end{array}\right\}$ oxidized and then dissolved in a liquid consisting of 100 grms. water and 30 grms. hydrochloric acid (spec. grav. 1·128), gave 0·958 grm. oxide of zinc = 0·769 zinc after treatment of the solution with sulphuretted hydrogen. The sulphuret of copper dissolved in nitric acid and the oxide precipitated by potash gave 1·031 oxide of copper = 0·823 copper. Similar results were obtained when the quantity of free acid in the liquid was larger.

The author has likewise tested the method proposed by Rivot and Bouquet for separating these metals, and finds that it furnishes results which are still less correct. The alloy was dissolved in nitric acid, the dilute solution saturated with ammonia, fragments of caustic potash added in slight excess until the ammonia was expelled, and the oxide of copper separated by filtration and weighed. The alkaline liquid was then saturated with hydrochloric acid, and the zinc precipitated by carbonate of soda.

A mixture of $\left\{\begin{array}{l}\text{zinc} = 0{\cdot}650 \text{ grm.}\\ \text{copper} = 0{\cdot}672 \text{ grm.}\end{array}\right\}$ gave—

0·803 grm. oxide of zinc, equivalent to 0·645 grm. zinc;
1·858 grm. oxide of copper, equivalent to 0·685 grm. copper.

The quantity of zinc was therefore too small by 0·76 per cent., and that of copper too large by 1·91.

The author then applied Rivot and Bouquet's method to the separation of the metals contained in the precipitates produced by sulphuretted hydrogen in the experiments 1, 2, 3, and obtained such quantities of zinc as would make up the true per-centage on addition to the portion remaining in solution after treatment in the first instance with sulphuretted hydrogen.—*Journ. für Prakt. Chem.*, vol. lvii. pp. 184–188.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Sulphurets which are decomposable by Water, followed by general Considerations on the Production of the Sulphurous and Siliceous Waters. *By* M. E. FREMY.

THE author, some time since, announced that he had discovered a method of obtaining with facility all the sulphurets which are decomposable by water. These compounds had, up to that time, been merely anticipated by chemists, or produced in small quantity by the action of the vapour of sulphur upon substances such as boron, silicon and aluminium, which are themselves difficult of preparation.

The object of this memoir is to make known the properties and composition of these sulphurets, and to show that they possess interest in a geological point of view.

The body which he first examined was the *sulphuret of silicon.* The result of his experiments is, that this sulphuret is formed in all cases when silex, whether free or combined with bases, is submitted to the action of sulphuret of carbon at a high temperature. Silex when free is attacked more readily than when in combination; yet felspar and vitreous substances furnish sulphuret of silicon in abundance when heated in the vapour of sulphuret of carbon; the action is facilitated by the presence of charcoal. The modification of silex which constitutes quartz produces sulphuret of silicon, but more slowly than that prepared by chemical processes, and which is soluble in alkaline solutions.

Sulphuret of silicon forms long silky needles; it is not reducible by hydrogen; moist air decomposes it completely, even at ordinary temperatures, changing it into anhydrous silica, which presents the same crystalline form as the sulphuret of silicon. The product of this curious transformation is not quartz, for the silica thus obtained is still soluble in alkalies.

When very pure sulphuret of silicon is allowed to fall into water, it produces a brisk effervescence of hydrosulphuric acid, and forms hydrate of silica, which remains entirely dissolved in the water. This siliceous water, of which the properties are fully treated of by the author in his memoir, is remarkable for its great stability when it is sufficiently diluted; it may be kept for months without depositing its silica. In certain circumstances this water produces gelatinous silica, which hardens on drying, and which, according to the author's analyses, contains 9 per cent. of water; it must be repre-

sented by the formula $(SiO^3)^2$, HO; it is interesting to observe that this hydrate approaches the opals, which often contain 9–10 per cent. of water. The author has also observed, that all hydrates of silica, when calcined in the furnace, change into substances presenting the physical and chemical properties of uncrystallized quartz; this transformation is an important fact in mineralogy.

Sulphuret of silicon, therefore, in contact with water, gives rise to two phænomena, interesting in a geological point of view, namely, the production of siliceous water, which may serve to explain certain siliceous incrustations; the other, the formation of a water containing sulphuretted hydrogen, presenting an analogy with that of some natural springs. In determining the products of this action, the author has analysed the sulphuret of silicon, for which he gives the formula SiS^3.

Sulphuret of Boron, like sulphuret of silicon, presents interest in a geological point of view. The author obtained it by passing sulphuret of carbon over a mixture of boracic acid and charcoal heated to a bright red heat; in this case the presence of the charcoal is necessary, as the boracic acid alone is not decomposed by the sulphuret of carbon.

This sulphuret is solid, of a yellowish-white colour, not very volatile, but readily carried off by vapours; it crystallizes in silky tufts; its odour is at once sharp and sulphurous; it is not reducible by hydrogen; it corresponds with boracic acid, its formula being BoS^3. In contact with water, it is decomposed with great rapidity, producing boracic acid and sulphuretted hydrogen, and frequently a deposit of sulphur, from which it might be supposed that there exists a sulphuret of boron corresponding to a higher degree of oxygenation than boracic acid.

Sulphuret of Aluminium was formed by exposing alumina, heated to bright redness, to the action of sulphuret of carbon; the presence of charcoal is useless in this case. This sulphuret is not volatile, and presents the appearance of a melted vitreous mass; water decomposes it, disengaging sulphuretted hydrogen and producing alumina, which is precipitated completely. Heated to redness in a current of watery vapour, it is decomposed, and furnishes anhydrous alumina in the form of small transparent grains possessing the hardness of corundum, but not regularly crystallized. It corresponds with alumina, its formula being $Al^2 S^3$.

Sulphuret of Magnesium is readily prepared by passing the vapour of sulphuret of carbon over magnesia heated to redness. It is not volatile; it is slightly soluble in water, which decomposes it, but more slowly than the preceding sulphurets; it corresponds with magnesia, its formula being MgS.

The author did not succeed in preparing *sulphuret of glucinium* in this manner. Glucina appears to be the only base which resists the action of sulphuret of carbon.

Zircon, placed in a charcoal crucible, was decomposed at a red heat by sulphuret of carbon, giving *sulphuret of zirconium*, which crystallized in beautiful steel-gray scales.

Crude yttria, submitted to the action of sulphuret of carbon, gave the sulphurets of the three metals existing in crude yttria,—*yttrium*, *erbium* and *terbium*.

Lastly, the oxides of iron, zinc, tin, lead, copper, &c., treated in the same manner, furnished metallic sulphurets, which are remarkable generally for their fine crystalline forms.

The sulphuret of carbon therefore decomposes nearly all oxides, and may be regarded as the most energetic of known agents of sulphurization.

After determining the properties and the composition of the sulphurets which are decomposable by water, the author enters upon the question, as to whether these sulphurets exist in some formations, and whether they do not then assist in the formation of the natural mineral waters. He considers that as the production of these sulphurets has hitherto been regarded as very difficult, it is not surprising that no one should have supposed them capable of playing an important part in natural phænomena, and that the production of sulphurous waters should have been accounted for generally by the action of reducing agents upon sulphates; but now that it is shown that these compounds may be formed without difficulty, it may readily be supposed that they exist in the veins which contain other metallic sulphurets. If this be admitted, it may be supposed that they may serve, in some cases, at any rate, as the source of sulphurous mineral waters.

At the same time, he does not suppose that these sulphurets result from the action of sulphuret of carbon upon the oxides of the metals, as in his experiments; but that under the circumstances of pressure and temperature, of which the influence at certain depths may be admitted, agents such as the sulphurets of arsenic and antimony may have had the same effect as the sulphuret of carbon in changing oxygenated substances into sulphurets decomposable by water.—*Comptes Rendus*, Jan. 24, 1853, p. 178.

Upon Palladamine. By Dr. Hugo Müller.

[Continued from p. 248.]

We now come to palladdiamine and its compounds. After Fischer had discovered that the red ammoniochloride of palladium dissolved without colour in caustic ammonia, Fehling found that 100 parts of the yellow variety (chloride of palladamine) took up between 15 and 16 parts of dry, and with decolorization from 24 to 24·7 of moist ammoniacal gas; he also found that the compound thus formed is readily soluble in water, and that it may be obtained from this solution in colourless crystals.

The first compound corresponds with the formula $PdCl+2NH^3$; the second is the same with 1 equiv. water.

When the author had ascertained the true nature of the yellow palladium salt, it was easy to see that a salt of a second palladium base was present, analogous to the chlorine compound of the second

platinum base discovered by Reiset; for if, according to Professor Wöhler's proposition, we transpose the formula thus,

$$N\left\{\begin{matrix}NH^4\\H\\H\\Pd\end{matrix}\right\}Cl,$$

we have the composition of Reiset's platinum salt, only with palladium substituted for platinum.

From the behaviour of this salt and the compounds produced from it, it appears that this supposition is perfectly well founded, and that there is consequently an ammonia base in which 1 equiv. of hydrogen is replaced by 1 equiv. of palladium, and a second by 1 equiv. of ammonium, just as in æthylamine and methylamine atoms of hydrogen are replaced by the compound organic radicals.

The basic oxide of this compound, which corresponds to ammonia, by analogy with the names æthylamine, methylamine, &c., already in use, should properly be called *ammonpalladamine*; but as this might readily be taken to apply to a common ammonium salt, the author has given the substance the name of *palladdiamine*.

Palladdiamine is always produced when a salt of palladium or of palladamine is treated with an excess of ammonia. By the evaporation of the colourless solution, the salt of palladdiamine is obtained in colourless crystals. In this manner the above-mentioned chlorine compound is readily procured in colourless prisms by the solution of the yellow chloride of palladamine in caustic ammonia, occasionally adding ammonia to supply the loss by evaporation.

To prepare the base from this, the author gradually added freshly-prepared oxide of silver. Chloride of silver was immediately formed, and the fluid became strongly alkaline. It had indeed acquired a slight odour of ammonia; but this, instead of increasing by boiling, disappeared entirely, whilst some chloride of silver, which had become dissolved, separated. After evaporation, the solution on cooling solidified into a mass of very long colourless prisms, which had an alkaline reaction; but, on closer investigation, it was evident that this substance contained oxide of silver, and thus appeared to be a compound of the oxide with palladdiamine.

As this small quantity of silver could not be got rid of by the addition of chloride of palladdiamine, the author proceeded to isolate the base from the sulphate by means of hydrate of baryta. The sulphate of palladdiamine was prepared by adding an excess of ammonia to a solution of protosulphate of palladium, and boiling the mixture. The sulphuric acid was then precipitated by hydrate of baryta, and a small quantity of ammonia, arising from a little sulphate of ammonia which was formed, removed by heat. In this manner, a pale yellow fluid, of a strong alkaline reaction and free from baryta and ammonia, was obtained; and this, on evaporation, left the base in the form of a crystalline mass. It had, however, suffered partial undecomposition.

Its solution is inodorous, reacts strongly alkaline, and precipitates

the bases from the salts of copper, iron, cobalt, nickel and alumina. It does not precipitate the silver salts.

When it is strongly boiled, a little ammonia is evolved, whilst the solution acquires a yellow colour, probably in consequence of the formation of palladamine. It is decomposed with remarkable ease by the presence of organic matters, which it may acquire during its filtration through paper; this gives it a brown colour. When heated above 212° F., the dry base first of all becomes yellow; it then fuses, and becomes decomposed with a slight detonation. Heated to the boiling-point with a solution of muriate of ammonia, it produces evolution of ammonia from the latter; the fluid does not acquire a yellow colour. When exposed to the air, it absorbs carbonic acid, but not so rapidly as palladamine.

When exactly saturated with acids in the cold, it forms salts, without undergoing any decomposition. An excess of acids, however, especially in the case of the hydracids, immediately effects its division into ammonia and palladamine, particularly when heat is applied.

Carbonate of Palladdiamine.—The pure base, as has already been stated, gradually absorbs carbonic acid from the air, and dries into a crystalline crust, which effervesces strongly with acids.

This salt is most readily obtained by the decomposition of the chloride by carbonate of silver; although when prepared in this manner, it is not quite free from silver.

Carbonate of baryta, added to a solution of sulphate of palladdiamine, gives a precipitate of sulphate of baryta, and a colourless solution, which crystallizes when brought to a proper degree of concentration.

This salt is also formed by the spontaneous decomposition of the cyanate of palladamine.

Carbonate of palladdiamine crystallizes in beautiful, shining, colourless, prismatic crystals, which become yellow superficially in air containing acids; at a few degrees above 212° F., it changes to a yellow salt. Its solution is colourless and strongly alkaline; it precipitates salts of copper, silver, baryta and lime, and gives no murexide reaction.

Sulphite of Palladdiamine, $\left\{\begin{matrix}NH^4\\H\\H\\Pd\end{matrix}\right\}NO, SO^2$.—It has already been stated of the sulphate of palladamine, that when that salt is brought in contact with ammonia, a colourless crystalline salt, which is difficult of solution, is formed; this is sulphite of palladdiamine.

If sulphurous acid is added to a solution of free palladdiamine, a precipitate of this salt is formed, either immediately or after a short time.

It forms small prismatic crystals, which cannot be more exactly determined on account of their minuteness; it is characterized by the difficulty with which it dissolves in water, by its insolubility in alcohol, and its stability. It remains unchanged at a temperature of 257° F., and only becomes yellow at about 392° F.

Boiled with concentrated acids, it evolves sulphurous acid, and forms salts of palladamine and ammonia with the acid employed. Its analysis gave—

Ammonia	27·10	1	26·66
Palladium	42·15	1	41·80
Sulphuric acid	24·92	1	25·30
Oxygen	..	1	6·24

This analysis was effected in the following manner:—

The salt, dried at 248° F., was distilled in an apparatus adapted to the purpose, with an excess of a highly-concentrated solution of potash; the ammonia thus obtained was passed into watery muriatic acid, and determined as ammoniochloride of platinum. The sulphurous acid was separated from the residue as sulphate of baryta, after the sulphurous acid had been converted into sulphuric acid by the addition of concentrated nitric acid. The palladium was precipitated as iodide of palladium, and obtained for determination in the metallic state by exposing this to a red heat.

Sulphate of Palladdiamine.—When ammonia is added in excess to a solution of sulphate of palladium, the brown precipitate which is at first thrown down becomes redissolved, and sulphate of palladdiamine is formed together with some sulphate of ammonia. The ammoniacal salt may be got rid of by treating the solution with a little hydrate of baryta. The concentrated solution furnishes colourless prismatic crystals, which are readily soluble in water, but insoluble in alcohol; with muriatic acid they form chloride of palladamine.

Chloride of Palladdiamine, $\left\{\begin{matrix}NH^4\\H\\H\\Pd\end{matrix}\right\}$N, Cl.—The preparation of this salt has been already described. It crystallizes in large, colourless, nearly rectangular four-sided prisms, which belong to the klinorhombic system. At 248° F. it loses 1 equiv. of ammonia and 1 equiv. of water, and becomes converted into chloride of palladamine. If any acid be added to a solution of this salt, the fluid acquires a golden-yellow colour, and deposits crystalline chloride of palladamine. Even carbonic acid passed into the fluid to saturation, separates small quantities of the latter salt after the lapse of a few hours.

According to Fehling's analysis, the crystallized hydrous salt contained—

Nitrogen	21·041	21·416	21·46
Hydrogen	5·388	5·698	5·21

According to the same author, 100 parts of yellow chloride of palladium took up 24·6 parts of ammonia instead of 24·7, which represents 1 equiv. The crystallized salt also contains 1 equiv. of water, with which the ascertained amount of hydrogen sufficiently agrees.

Bromide of Palladdiamine.—When an excess of ammonia is added to a solution of bromide of palladium, or when ammoniobromide of palladium or bromide of palladamine is dissolved in ammonia and

the colourless solution concentrated, remarkably large, well-formed, nearly colourless, generally tabular crystals of bromide of palladdiamine separate.

The crystals are short klinorhombic prisms, with a larger lateral angle of 98°; their terminal facets are set at an angle differing but little from a right angle.

In pure air this salt is tolerably stable; the action of acid vapours, however, readily causes it to lose its lustre, and produces a yellow superficial coating of a salt of palladamine.

In other respects this salt behaves in a very similar manner to the chloride, and is only distinguished from this by the form of the crystals; these in the bromide being of a short tabular form, whilst in the chloride they are rather of an elongated prismatic shape.

Iodide of Palladdiamine, $\left\{\begin{matrix}NH^4\\H\\H\\Pd\end{matrix}\right\}$N, I.—The solution of iodide of palladium or of iodide of palladamine in hot concentrated ammonia, evaporated in an atmosphere of ammoniacal gas, or with constant additions of ammonia, furnishes colourless crystals. If ammoniacal gas be passed over iodide of palladium, this acquires a white colour, 100 parts of the salt absorbing 19·4 parts of the gas, that is to say, 1 equiv. of the salt takes up 2 equivs. of ammonia.

The crystals, when exposed to the air, lose ammonia rapidly, and acquire a yellowish colour; they also become yellowish-red in the course of half a year when kept in closed vessels. Fehling's analysis of this salt agrees very well with the formula.

Fluoride of Palladdiamine.—The mode of preparation of this salt has already been given under fluoride of palladamine. If, before the decomposition of the latter has commenced, ammonia be added to the solution obtained by the decomposition of fluoride of silver by chloride of palladamine, the whole of the palladamine salt is obtained on evaporation as fluoride of palladdiamine. This salt forms colourless crystals of the form of those of the bromide; these are permanent in the air, and dissolve readily in water, but attack glass even in the driest possible state. Hydrochloric, hydriodic, and hydrobromic acids throw down the corresponding palladamine salts, after a considerable time in the cold, but instantaneously when heated. On the other hand, when an excess of hydrofluoric acid is added to a solution of this salt, no precipitate of the corresponding palladamine salt is produced either by heat or cold.

Silicofluoride of Palladdiamine.—When fluosilicic acid is added to the solution of a salt of palladamine, a precipitate of colourless, rather large, scaly crystals, of a pearly lustre, is soon produced; these are insoluble in alcohol, slightly soluble in cold, but readily in hot water, separating again on cooling in large laminar crystals. This substance, from its general behaviour, is silicofluoride of palladdiamine. When an excess of fluosilicic acid is added to it, neither a precipitate nor coloration is produced to indicate the formation of a palladamine salt. This salt consequently behaves exactly like the

fluoride, and with this and the sulphite is the most stable salt of the base.

Cold muriatic acid only produces a yellow colour, and precipitation of chloride of palladamine after the lapse of considerable time; when heated, it effects this immediately.

When heated to 320° F., the crystals become yellow; at a higher temperature they are completely decomposed, leaving a residue of metallic palladium of the form of the salt.

The following experiment was made with the view of producing, by the combination of palladamine and cyanic acid, a urea in which one-fourth of the hydrogen should be displaced by palladium.

For this purpose, chloride of palladamine was brought in contact with cyanate of silver and water. Even in the cold, the yellow colour of the salt of palladamine disappeared, and the fluid became pale yellow. An interchange of elements consequently took place, and cyanate of palladamine must exist in the solution, as indeed was proved by the reaction of palladium. After the two salts had acted upon each other for a sufficient time, the fluid was filtered off; but in attempting to concentrate this, with a view to crystallization, the temperature employed, although less than 104° F., was sufficient to effect a change in the mixture, for the fluid became decolorized without turbidity, but with a sudden and violent evolution of carbonic acid gas. This effervescence of carbonic acid was soon ended, and the fluid could be concentrated without any further decomposition. On slow evaporation, very shining, colourless, prismatic crystals separated.

This salt effervesced with acids, and with muriatic acid gave the characteristic precipitate of chloride of palladamine. Further investigation showed that it was carbonate of palladdiamine.

It follows therefore from this experiment, that the cyanate of palladamine, like the cyanates of the alkalies, is very readily decomposed when in contact with water, becoming converted into carbonic acid and palladdiamine, according to the following equation:—

$$NH^3\,PdO + C^2\,NO + 3HO = N^2\,H^6\,PdO + 2CO^2,$$

the half of the carbonic acid formed being set free. It still remains to be seen how the base and acids behave towards one another in the absence of water.

Palladæthylamine, $\left\{\begin{matrix} C^4\,H^5 \\ H \\ H \\ Pd \end{matrix}\right\}$ N, Cl.—If a solution of chloride of palladium be mixed with æthylamine free from ammonia, a reddish-yellow crystalline precipitate is produced, which is probably $PdCl + C^4\,H^7\,N$. It is soluble in an excess of æthylamine. If muriatic acid be added to the colourless solution, a pale yellow precipitate is produced, which after some time becomes crystalline and dark yellow. Microscopic examination showed it to consist of prismatic crystals, mostly united in a cruciform position, and very different in form from those of the corresponding salt of palladamine. This substance is without doubt the

Chloride of Palladdiæthylamine, $\left\{\begin{matrix} C^4\,H^5 \\ C^4\,H^7\,N \\ H \\ Pd \end{matrix}\right\}$NCl.—It is dissolved by æthylamine, giving a colourless fluid, from which a salt in colourless prisms is readily obtained by evaporation. From the mode of its formation and its reactions, this substance must have the above formula.

Palladæthyldiamine, $\left\{\begin{matrix} C^4\,H^7\,N \\ H \\ H \\ Pd \end{matrix}\right\}$N, Cl.—If watery æthylamine be poured over chloride of palladamine, the yellow colour of the latter disappears immediately; by the application of a gentle heat, it is dissolved, forming a colourless fluid, which on cooling deposits colourless crystals presenting the greatest resemblance to chloride of palladamine. Muriatic acid throws down chloride of palladamine from the solution of this salt.

Palladanilamine, $\left\{\begin{matrix} C^{12}\,H^7 \\ H \\ H \\ Pd \end{matrix}\right\}$NCl.—Aniline diffused in water, added to a solution of chloride of palladium, throws down a pale yellow crystalline precipitate, which after filtration resists the action of the air, and is insoluble in an excess of aniline. This substance is very probably the chloride of palladanilamine.—*Inaugural Dissertation, Göttingen*, 1853.

On the Adulteration of the Citrate of Iron and Quinine of Commerce. By C. Greville Williams*.

Physicians not yet being agreed as to the identity of action on the system of quinine and its accompanying alkaloids, it is unnecessary to insist on the fact, that until the question has been settled by decisive experiments, practitioners should be aware of the value of the preparations they are administering to their patients.

A quantity of beautifully "sealed" citrate of iron and quinine having been sent to me, with a request for examination, the percentage of quinine being suspected to be below the proper quantity, it was examined thus:—

100 grs. dissolved in the least possible quantity of distilled water, the solution filtered from a small quantity of dirt (!), the filter carefully washed, and the filtrate precipitated by a very small excess of ammonia. The precipitate was washed as much as was safe with water containing a little ammonia; it was then dried on the water-bath at 212°. After being exposed to this temperature for some time, it was observed that the precipitate, instead of melting to the paper as quinine does, remained in the form of a powder; it was therefore weighed, and found to be 10·4 grs.; on digestion in the cold with æther, this was reduced to 5·1. The portion dissolved

* Communicated by the Author.

proved on examination to be quinine; and the portion separated by the filter, as was suspected from its infusibility at 212°, turned out to be cinchonine.

The scales therefore consisted of—

Citrate of sesquioxide of iron and ammonia ..	89·6
Quinine	5·3
Cinchonine	5·1

The per-centage of quinine paid for by the pharmaceutist was 12·5 per cent.

On the Combinations of Boracic Acid and Water with the Oxides of Lead and Copper. *By* H. Rose.

Boracic acid and water combine with oxide of lead in the most varied proportions; with few other compounds can the influence of water at different temperatures and in various quantities be so well demonstrated as with these. Oxide of lead yields considerably to the alkaline earths in its affinity for boracic acid, for these principally unite with boracic acid and water only in certain proportions.

When solutions of equivalent proportions of nitrate of lead and neutral borate of soda, NaO, BO^3, are mixed together in the cold, neutral borate of lead is not obtained, but a precipitate of the composition $3PbO\,BO^3 + HO + PbO, HO + HO$; this, however, loses still more boracic acid by washing with cold water, and changes thus into $PbO\,BO^3 + HO + PbO\,HO$. If the solutions of the two salts be brought into contact whilst hot, the unwashed precipitate is of the composition $PbO, BO^3 + HO + PbO, HO$, but when washed with hot water, $3(PbO, BO^3 + HO) + 5PbO\,HO$.

By the decomposition of cold concentrated solutions of nitrate of lead and biborate of soda a precipitate is produced of the composition $PbO(BO^3)^2\,HO + 8(PbO\,BO^3\,HO)$, which thus very nearly approaches neutral borate of lead. By washing it becomes quite neutral, and is then $PbO, BO^3\,HO$. Very dilute cold solutions give a precipitate of $5PbO\,BO^3\,HO + 4PbO\,HO$.

By the decomposition of hot concentrated solutions of these salts, the precipitate $5(PbO, BO^3\,HO) + PbO\,HO$ is obtained, which by washing with hot water is changed into the compound $3(PbO, BO^3\,HO) + PbO\,HO$. With very dilute hot solutions, the precipitate $PbO, BO^3\,HO + PbO\,HO$ is produced, which, of all the compounds formed by the action of common borax upon salts of lead which were examined, contains most lead compared with the boracic acid.

Water expels a portion of the boracic acid from the salts of this acid with oxide of copper, still more readily than from its lead compounds. It is even possible, by employing a large quantity of water, and assisting the action of that fluid by an elevated temperature, to separate at last all the boracic acid from the oxide of copper.

If concentrated solutions of equivalent proportions of sulphate of copper and neutral borate of soda be mixed together while cold, a precipitate of $5(CuO\,BO^3 + HO) + CuO\,HO$ is obtained; this however is mixed with sulphate of soda and insoluble basic sulphate of

copper. After washing with cold water, the compound consists of $2(CuO\ BO^3 + HO) + CuO\ HO$, mixed with some basic sulphate of copper. Hot concentrated solutions of the two salts give a precipitate of the composition $5(CuO\ BO^3 + HO) + 6CuO\ HO$, mixed with sulphate of soda and basic sulphate of copper. If this be washed with hot water, it has essentially the composition $(4CuO\ BO^3\ HO) + 7CuO\ HO$, mixed or combined with $2(CuO)^3\ SO^3$.

Biborate of soda and sulphate of copper in their cold concentrated solutions give the compound $20(CuO\ BO^3\ HO) + 13(CuO\ HO)$ mixed with $(CuO)^3\ SO^3$ and $2NaO\ SO^3$, which loses boracic acid by washing with cold water, and becomes $CuO\ BO^3\ HO + CuO\ HO$, mixed with some basic sulphate of copper. Hot concentrated solutions also give the compound $CuO\ BO^3 + CuO\ HO$ mixed with sulphate of soda and basic sulphate of copper; this however loses boracic acid even by washing with cold water, and becomes $CuO\ BO^3 + 3CuO\ HO$ mixed with some $(CuO)^3\ SO^3$, and still less $NaO\ SO^3$; but after washing with hot water, it is $4(CuO, BO^3\ HO) + 5CuO\ HO$ mixed with $2(CuO)^3\ SO^3$ and some sulphate of soda.

Cold dilute solutions of the salts give a compound $2(CuO, BO^3, HO) + 3(CuO, HO)$, but with hot dilute solutions so much boracic acid is extracted from the precipitate by the large quantity of water, that after washing it has the composition $CuO\ BO^3\ HO + 10CuO + 8HO$. If the boiling be continued for some time with the dilute solutions, a precipitate may be at last obtained, from which all the boracic acid is extracted, and which consists essentially of $10CuO + 3HO$.—*Monatsb. der Akad. der Wissensch. zur Berlin*, 1852, p. 549.

On the Preparation of Nitro-prusside of Sodium.
By A. Overbeck.

The salt discovered by Playfair, which is produced with evolution of oxide of nitrogen, cyanogen, nitrogen and carbonic acid, by the action of nitric acid upon prussiate of potash, is only separated with difficulty from some substances which are also dissolved in the fluid. From this fluid, which is brown, nitrate of potash and oxamide separate; and after neutralization with carbonate of soda and sub sequent heating, a green or brown precipitate is deposited.

The separation of Playfair's salt from the nitrate of potash by Playfair's process has given the author no satisfactory result, because the selection of the two kinds of crystals is very wasteful of time. Kyd also appears to have succeeded no better, since he has adopted another course. The author could not find the point at which the nitroprusside of sodium first crystallized, by trying the fluid on the sand-bath with the thermometer at all temperatures from 176° F. downwards. By spontaneous evaporation also he always obtained a mixed crystallization, both salts forming in intimate contact. The method given by Kyd for the preparation of the nitroprusside of copper has also its particular difficulty. Without taking into consideration that the smallest excess of caustic soda in the decomposi-

tion of the nitroprusside of copper contaminates the product with an alkaline ferrocyanide, a pure green precipitate is not always obtained on precipitation with sulphate of copper; it is frequently reddish from ferrocyanide of copper, the formation of which is not to be avoided when there is an excess of carbonate of soda, and which is intimately connected with the brown colour of the precipitate formed by boiling the neutralized fluid.

According to the experiments made by the author with reference to Playfair's further statements, the following method is adapted to furnish the salt pure:—

5½ parts of commercial nitric acid, diluted with an equal weight of water, are poured over 4 parts of pounded prussiate of potash in a retort; after solution has taken place, which is generally completed in about ten minutes when the acid is of the usual degree of concentration, with strong evolution of the gases described by Playfair and the production of a coffee-brown colour, the retort is placed upon the water-bath until a drop of the fluid gives a dingy green instead of a blue precipitate with a solution of sulphate of iron. The solution is allowed to cool, by which means a large quantity of nitrate of potash is separated, from which the green mother-liquor is poured away; from this all nitrate of potash is separated by repeated concentration. The fluid is then neutralized with carbonate of soda while being heated on the water-bath, taking care only to add the carbonate as long as a pure blue precipitate is produced. This is collected on a filter and washed. From the united filtrates the substance is obtained in the most perfect purity by spontaneous evaporation. The ruby-red prismatic crystals are washed with water, and dried between blotting-paper.

The crystals, as well as the solution, are best preserved in black bottles. At any rate, the solution must be carefully kept from the sunlight.—*Archiv der Pharm.*, lxxii. p. 270.

On the Oil of Hops. By Dr. R. Wagner.

The author, in examining this oil, has arrived at the following results:—

1. That the oil does not contain sulphur, and belongs to the group represented by the general formula $C^{10} H^{8}$.

2. That it is a mixture of camphene, $C^{20} H^{16}$, and the bihydrate of this compound, $C^{20} H^{18} O^{2}$. Oxidized bihydrate appears likewise to be present in small quantity.

3. The oil is but slightly soluble in water, requiring more than 600 times its weight.

4. It has no narcotic action.

The oil employed by the author in his investigation was prepared with great care from hops grown in the neighbourhood of Nuremberg by distillation with water. The product amounted to 0·8 per cent. of the air-dried hops.

The pure oil has a light brownish-yellow colour, a powerful but not intoxicating odour, and a burning slightly-bitter taste, somewhat

resembling thyme. Its specific gravity is 0·908 at 60°·8 F. It scarcely reddens litmus-paper; but when this is saturated with the oil and exposed to the air, it becomes decidedly red.

In order to prove chemically the absence of sulphur, about 1 grm. of the oil was mixed with dry carbonate of soda, and the whole treated with melted nitrate of potash. The solution of the cooled mass gave no precipitate with chloride of barium.

On digesting an alcoholic solution of the oil with fresh precipitated oxide of lead, no sulphuret was formed. An aqueous solution of the oil, digested with a bright silver coin, produced no change of the surface.

According to the statements of Payen and Chevallier, the oil of the flowers and that of the entire catkins contain sulphur. Wagner finds, however, that this is incorrect, and is of opinion that these chemists must have operated upon oil obtained from hops which had been bleached by sulphurous acid. Several samples of hops which had been thus bleached were distilled with water, and the distillate in every instance showed the presence of sulphur, while that from unbleached hops gave no reaction.

The author points out this circumstance, the more especially since the examination of hops for sulphurous acid is frequently the subject of chemical jurisprudence. Its presence may be ascertained most satisfactorily by treating the suspected hops with zinc and dilute sulphuric acid, and passing the gas disengaged into a solution of basic acetate of lead.

The hop-oil, dried over chloride of calcium, evaporates at a temperature below the boiling-point of water. It commences to boil at 257° F., the temperature rising until it reaches 347° F., when it remains stationary for some time, and one-sixth of the oil passes over. The distillate A was colourless, clear, and possessed an odour somewhat resembling rosemary. The portion B, which passed over between 347° and 457° F., amounted to about one-half of the whole, was likewise colourless, and possessed the odour of hops. That which passed over between 437° and 457° F. was of a yellowish colour. The residue in the retort was brownish and terebinthinate. It amounted to about one-sixth of the oil.

It follows from these facts that the oil is a mixture. When treated with an ammoniacal solution of silver, it does not cause reduction; consequently it is not an aldehyde. The dry oil is unaltered by potassium until sufficient heat is applied to melt the potassium, when a disengagement of gas takes place, and the oil becomes brown and thick. Dry iodine colours the oil brown; on applying heat, the action becomes violent, and a brown resin is formed. Bromine produces a similar effect. The oil does not yield chloroform with chloride of lime, or a crystalline compound with sulphite of ammonia. With an alcoholic solution of potash, the oil becomes brown; alcohol and an oil smelling of rosemary pass over on distillation. Subsequently there is a disengagement of gas (probably hydrogen), and carbonate of potash mixed with the potash salt of a

fatty acid remain. This fatty acid appears to be a mixture of caprylic and pelargonic acids.

The oil which passed over during this reaction resembled the above-mentioned portion A. It was not acted upon when heated with potassium, and boiled between 315° and 356° F. Analysis gave—

Carbon	88·9	5	88·23
Hydrogen	11·9	4	11·77

This substance therefore belongs to the class of camphenes. It absorbs hydrochloric acid, forming a brownish liquid, which does not solidify even at a low temperature.

The oil B was submitted to fractional distillation, and the portion which passed over, while the temperature remained constant at 406° F., gave on analysis—

Carbon	78·19	20 =	120	77·92
Hydrogen.....	12·00	18	18	11·69
Oxygen.....	..	2	16	10·39

This oil undergoes a gradual oxidation, and when exposed to the air forms a tenacious mass. On distillation with fused chloride of zinc, a colourless oil passes over, which perfectly resembles, and appears to be identical with the hydrocarbon.

If then this hydrocarbon really originates from the oxygenated oil by the separation of the elements of water, it will have the formula—

$$C^{20}H^{16},$$

and the oxygenated oil the formula—

$$C^{20}H^{16}+2HO.$$

The oil $C^{20}H^{18}O^{2}$ is isomeric with Borneo camphor, cajeput and bergamot oils, and the aldehyde of campholic acid, $C^{20}H^{18}O^{4}$. By treating the oxygenated part of hop-oil with nitric acid, the author was unable to obtain anything more than a brittle yellow resin.

The oil C contains more oxygen than B. Analysis gave 73·8 per cent. of carbon.

The author has, together with V. Bibra, instituted a series of experiments on the physiological action of the oil; and they have ascertained that it has no narcotic effect, and corresponds with other volatile oils. A rabbit bore a dose of 20 drops without loss of appetite or any other sign of discomfort.

Rochleder's investigations have shown that the so-called active principles are common to all the members of a natural family. Both hops and hemp belong to the Urticaceæ; both plants have a great analogy in a physiological point of view. Now since the narcotic effect of beer results from a yet unknown constituent of the hop, probably an organic base, and as hemp, according to the above principle, would contain the same constituent, it would perhaps be theoretically correct to grow hemp instead of hops for the purpose of communicating to beer its bitter taste and narcotic properties. The bitter of hemp closely resembles that of the hop. In an agri-

cultural point of view, this would be very advantageous, for besides the fact that the growth of hemp is less dependent than the hop upon meteorological conditions, the former can, after the extraction of the soluble constituents, be employed in making yarn. The oriental nations have since the most remote period been acquainted with the narcotic properties of the *Cannabis indica*; the famous nepenthe of the ancients is said to have been prepared by decocting the hemp leaves. At the present day the Arab employs his Haschisch* for the same purpose. In the Persian taverns in the country, an infusion of the larger leaves and capsules of hemp is used, under the name of *Subjee* or *Sidhee*, to relieve the fatigue of travellers. In Egypt, hemp-extract is frequently taken with strong coffee after dinner. The growers of hemp in this country are sufficiently aware that our hemp has likewise a narcotic property.

It follows from these remarks, that hemp as well as hops and opium are employed by the most different nations for the same purpose; and the remark of Knopp† is much to the point, that beer-drinking is, strictly speaking, analogous to the combined use of opium and spirituous liquors.

With regard to the chemical constitution of hops, we are without any trustworthy knowledge; and the same is true of the varieties of hemp, especially of the cause of the remarkable properties of *Cannabis indica* and *haschisch*.

The author is at present engaged in the investigation of the former subject.—*Journ. für Prakt. Chem.*, lviii. 6.

Photography on Stone. By MM. Barreswil *and* Lemercier.

The process proposed by the authors consists in preparing a negative on paper, and then producing a positive picture on lithographic stone. The negative is obtained by any method, the most rapid being preferable. The positive is produced by a fatty or resinous coating laid on the stone, and capable of being rendered soluble in some solvent by the action of light (and perhaps of oxygen). The negative is laid upon the lithographic stone thus prepared, and covered with a glass plate; the whole is then exposed to the sun, the stone washed with the solvent, and then treated by the ordinary processes of lithography. The authors have hitherto employed asphaltum for coating the stone, and sulphuric æther as the solvent. They expect in this manner to reproduce engravings, lithographs, &c.—*Comptes Rendus*, May 16, 1853, p. 878.

On the Preparation of Lakes by means of Chloride of Antimony.

Chloride of antimony, which is to be met with in commerce under the name of *Liquor Stibii muriatici*, may, according to a recent observation of Prof. Lampadius, be very well employed in the pre-

* Dr. Schroff points out in his 'Pharmacognosie,' 1852, p. 129, that the Haschisch which comes to Europe has a taste of hops.

† Technologie, vol. ii. p. 469.

paration of several lakes. By dropping it into decoctions of Pernambuco-wood, madder, Campeachy-wood, Quercitron-wood, and several other colouring matters, lakes, some of which are very fine, are produced.

From the infusion of cochineal in liquid ammonia, prepared in the cold, when a little pure vinegar is added to it, a large quantity of lake is obtained, which does not yield greatly in beauty to carmine.—*Schweiz. Gewerbeblatt*, vol. xi. p. 127.

Analysis of Pig Iron and Bog Iron Ore. By H. L. Buff.

Pig iron, of a nearly white colour, very hard and susceptible of polish, smelted with charcoal from bog iron ore at the Friedrich-Wilhelms-Hütte, at Gravenhorst in Westphalia, contained—

I. Pig iron.		II. Bog iron ore.	
Free carbon....	1·42 per cent.	Oxide of iron	65·443
Graphite	1·25 ...	Oxide of manganese	7·025
Silicon.....	0·61 ...	Phosphoric acid ..	3·306
Phosphorus	0·56 ...	Silica.....	9·219
Nitrogen	0·26 ...	Water	15·021
Manganese	1·41 ...		

Ann. der Chem. und Pharm. vol. lxxxiii. p. 376.

ANALYTICAL CHEMISTRY.

On the Determination of Copper and Nickel in Quantitative Analysis. By David Forbes, F.G.S.

Although the determination of these metals by the present methods, when properly conducted, must be considered quite accurate, still they are tedious, and are likewise attended with several sources of error, so as to render it desirable to endeavour by some simpler process to shorten the manipulation generally employed, as well as, if possible, to diminish the chances of incorrectness.

Both copper and nickel are usually weighed in the state of oxide, procured by precipitating their respective solutions by potash. This precipitation, if not conducted with great care, is liable to errors so considerable as completely to vitiate the results obtained, from the tendency which potash has to precipitate basic salts; so that the precipitate produced is not the oxide itself, but a compound of the oxide with potash, generally retaining in addition some of the solvent acid.

This compound, in the case of nickel and copper, is however decomposable by boiling water, and this property affords the means of obtaining the oxides in a pure state previous to ignition; it is, however, evident that some risk always exists of a portion not being perfectly decomposed by this washing, which should be conducted at a boiling temperature, and carried on without intermission until concluded. In cases where even a very small amount of organic

matter* is present, either in the solution, or, as frequently happens, in the potash employed, the precipitation is not complete, or rather a portion of the oxide is retained, dissolved in the solution, and is not precipitated by the further addition of potash.

Another objection also is, that when igniting the oxide, a portion of it may be reduced by the carbonaceous matter of the filter; this can, however, be readily obviated, either by prolonged ignition, or by moistening the oxide with nitric acid, and again igniting; but the operation is then necessarily more tedious.

When we likewise consider that copper and nickel are generally separated in the course of analysis by precipitation as sulphuret, we shall at once see the desirability of endeavouring to determine their quantities as directly as possible from that compound; and the following experiments were made with this object in view.

The first point inquired into was, whether the precipitated sulphurets of prolonged ignition, or rather calcination, could not be completely deprived of all their sulphur, and converted into oxides. The results obtained were, however, not at all satisfactory, as the sulphurets were never completely decomposed, and invariably yielded too high results, as may be seen from the following experiments:—

a. 3·75 grs. metallic copper, equivalent to 4·70 grs. oxide, yielded 5·47 grs. incinerated sulphuret, being an excess of 0·77 gr., or equal to 16·38 per cent. too much oxide.

b. 3·63 grs. metallic copper yielded 5·10 grs. instead of 4·55 grs. CuO; equal to excess of 0·55 gr., or 12·08 per cent.

c. 1·76 gr. copper, =2·20 CuO, gave 2·24 grs., an excess of 0·04 gr., or 1·81 per cent. too much.

d. 25·00 grs. of a mineral, containing by a previous examination 45·31 per cent. copper, afforded 17·64 grs. calcined sulphuret, equivalent, if reckoned as CuO, to 14·08 grs. metallic copper, or 56·32 per cent. This oxide, dissolved in nitric acid, and determined in the usual manner by precipitation by potash, with all precautions, gave 14·10 grs. CuO, equal to 11·25 grs. metallic copper, or 45·04 per cent.; so that in this case, if the ignited sulphuret had been considered as oxide, the quantity of copper present would have been over-estimated by more than 10 per cent.

The copper in all these cases was thrown down from its solution in nitric or hydrochloric acid by a stream of sulphuretted hydrogen, and washed with water impregnated with that gas.

Again, in repeating these experiments with nickel, equally unsatisfactory results were obtained; thus,—

4·98 grs. nickel, equivalent to 6·34 grs. NiO, afforded 6·96 grs. incinerated sulphuret; or an excess of 0·62 gr., equal to 9·79 per cent. too much.

10·35 grs. nickel, equal to 13·16 NiO, gave 13·27; equal to 0·11 gr. too much, or 0·82 per cent.

* This is particularly apt to take place if great care is not taken to incinerate the filter perfectly on which these metals had been precipitated previous to solution.

The nickel being in these cases precipitated from its solution by hydrosulphuret of ammonium.

It will also be noticed, that neither in the case of nickel or copper does the excess appear constant, but perfectly uncertain in amount. With the hope that the pure oxide would remain on treating the ignited sulphuret with nitric acid, in the same porcelain crucible in which it had been incinerated, evaporating to dryness, and again igniting, so as to drive off the sulphuric acid formed, this was tried, and

11·72 grs. of an alloy, containing by calculation 49·49 per cent. copper, was dissolved, the copper precipitated by sulphuretted hydrogen, washed and treated as above, yielded 7·74 grs. impure oxide, equal, if considered as CuO, to 6·179 metallic copper, or 52·72 per cent.; showing an excess of above 3 per cent., arising from undecomposed sulphate of copper.

Further trials, in which the oxides thus obtained were very strongly ignited, with a view to decompose thoroughly all sulphate present, afforded much better, and nearly, if not quite, accurate results; but the heat required was found inconveniently great, and considerable difficulty was found in decomposing the last traces of sulphate; in consequence, therefore, the method now about to be noticed was tried, and found much more convenient in practice, and to afford very accurate results.

Upon analysing the residue left after incinerating the sulphurets produced by precipitating these metals, it was found to consist of a mixture of the disulphuret and oxide of the metal, and containing a small amount of sulphate. This will be seen from the following results:—

a. 13·27 grs. incinerated sulphuret of nickel (precipitated by hydrosulphuret of ammonium), yielded on analysis—

Nickel	10·35
Sulphur	0·60
Oxygen	2·21
Sulphuric acid	0·11
	13·27

which by calculation will be equivalent to—

Nickel	2·21	
Sulphur	0·60	
		2·81 $Ni^2 S$
Nickel	8·08	
Oxygen	2·20	
		10·28 NiO
Oxide of nickel	0·09	
Sulphuric acid	0·11	
		0·20 $NiO\,SO^3$
		13·29

which shows a difference of only 0·02 gr. from the obtained results. Again, in the case of copper,

b. 2·24 grs. incinerated sulphuret of copper (precipitated by a stream of sulphuretted hydrogen) afforded—

Copper	1·760
Sulphur	0·058
Oxygen	0·392
Sulphuric acid	0·030
	2·240

which, upon calculation, is equivalent to—

Copper	0·229	
Sulphur	0·058	
		0·287 Cu^2S
Copper	1·537	
Oxygen	0·387	
		1·924 CuO
Oxide of copper	0·029	
Sulphuric acid	0·030	
		0·059 $CuO\,SO^3$
		2·270

or an excess of 0·03 gr. above the quantities experimentally found*.

As now the atomic equivalent of sulphur is exactly double that of oxygen, that of the disulphuret of a metal will of course be precisely the same as of its corresponding protoxide; and this fact consequently enables us at once to calculate the amount of copper or nickel contained in a mixture of the disulphuret and oxide, however variable the relative proportions of these compounds may be; and it becomes only necessary to remove the small amount of sulphuric acid present in the incinerated sulphurets, in order to determine the amount of the one or other metal present.

The addition of a small amount of pulverized carbonate of ammonia to the incinerated sulphuret (as soon as cold), and then carefully heating until all ammoniacal salts are expelled, seems completely to effect this object, as will be seen from the following results, obtained experimentally:—

a. 4·30 grs. metallic copper, precipitated by the electrotype, were dissolved, precipitated by sulphuretted hydrogen, and treated as above with all precautions. The mixture of $CuO + Cu^2S$ obtained amounted to 5·37 grs., whereas by calculation it should have been 5·38 grs.

b. 1·76 gr. same copper, similarly treated, yielded 2·21 grs. $CuO + Cu^2S$, whereas by calculation it should have afforded 2·204 grs.

c. 17·89 grs. of an alloy, containing by calculation 49·49 per cent. copper, treated as above, yielded 11·12 grs. $CuO + Cu^2S$, equivalent to 8·878 Cu, or 49·62 per cent. copper.

d. 7·61 grs. pure metallic nickel, precipitated from its solution by hydrosulphuret of ammonium, and treated as above, yielded 9·665 grs. $NiO + Ni^2S$, or equivalent to 7·607 grs. nickel.

* The equivalents for nickel and copper employed in the preceding calculations have been Ni = 29·57, Cu = 31·66, O = 8, S = 16.

e. A solution of 4·99 grs. nickel and 3·73 grs. copper was treated with sulphuretted hydrogen to separate the copper; the nickel, afterwards thrown down by hydrosulphuret of ammonium, and both determined as above, gave—

6·34 grs. $NiO + Ni^2 S = 4·98$ grs. metallic nickel, and
4·70 grs. $CuO + Cu^2 S = 3·75$ grs. metallic copper.

As these results appeared extremely satisfactory, it seemed not unlikely that this process could also be extended to the determination of cobalt; and, in consequence, 5·25 grs. pure metallic cobalt were dissolved in nitric acid, and neutralized by ammonia, then precipitated by hydrosulphuret of ammonium. The precipitated sulphuret, after washing, incineration, and ignition with carbonate of ammonia, weighed 8·98 grs.; and even after being several times successively heated with carbonate of ammonia, it weighed 8·68 grs., whereas by calculation it should only have yielded 6·67 grs. The residue, which was expected to have consisted of oxide and disulphuret, appeared quite pink, and aggregated together on each ignition, evidently containing a large amount of sulphate of cobalt, which seemed most strongly to resist decomposition; and therefore it does not appear probable that this method could be employed in the determination of cobalt.

From the results obtained with copper and nickel, it may be concluded that the process here described may safely be used in estimating these two metals; and, in a very large number of determinations of nickel, it has been found to afford the most accurate and satisfactory results.

In the case of copper, however, more attention must be paid to the details of the operation, as the protosulphuret of copper, especially in cases where free sulphur has been precipitated along with it, is very apt to aggregate together, or even fuse during the incineration (if this is not very carefully conducted), and consequently is less easily acted upon by the air during incineration; this must be avoided, and the oxide should also not be allowed to absorb hygrometric moisture before or during weighing.

It will be found most convenient to add the carbonate of ammonia to the incinerated sulphuret in the same crucible in which it had been ignited, or rather to cover the ignited sulphuret with four or five times its volume of this salt; and then, by means of a small agate pestle or glass rod, to break up all grains, and mix it well together by trituration, which can be easily effected without any loss whatever, as the superstratum of carbonate of ammonia effectually prevents any particles flying over the side of the crucible. This, with its cover loosely placed upon it, is now very gently heated until nearly all ammoniacal salts are expelled; then the heat is increased for an instant, and the whole, after cooling over sulphuric acid, is weighed and estimated as usual.—Jameson's *Edinburgh Journal*, July 1853.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Examination of Fusel Oil from Indian Corn and Rye.

By CHARLES M. WETHERILL, PH.D., M.D.

THE researches of Guckelberger, Bopp, Keller, and others, who obtained, by the fermentation and oxidation of nitrogenized substances, such as gluten, caseine, &c., the successive members of the series of acids, $C^n H^n O^4$, rendered it probable that such a succession might be detected in fusel-oil, by employing Liebig's method of isolating these acids, a method which enables small quantities of one of the group to be separated from larger quantities of the other members. It was also interesting to make an examination of fusel-oil obtained from the fermentation of Indian corn.

With respect to the history of fusel oil; as is well known, Dumas obtained it first from the fermentation of potatoes; Balard showed that with this the oil obtained from the fermentation of grapes was in its principal constituent (amylic alcohol) identical; and Medlock and Rowney showed the same to be the case with the fusel-oil of the English and Scotch grain distilleries.

With regard to the acids present in fusel oil, Mulder detected œnanthic, Kolbe margaric, and Rowney capric acid. Medlock, who examined a grain fusel-oil for an alcohol of one of the fatty acids, obtained nothing but alcohol, water and amylic alcohol. Kent (Am. Journ. Pharm., 1851, p. 354) examined a specimen of fusel-oil which contained acetic and valerianic acids, besides an æther, the acid of which was not isolated.

Wurtz (Comptes Rendus, xxxv. 310) has recently isolated from potato fusel-oil, butylic alcohol, boiling at 112° C.

In the subject of the present memoir, besides water and alcohol, formic(?)*, acetic, caproic(?), œnanthic(?), and caprylic acids were detected, together with a small quantity of oil of turpentine, which probably proceeded from the barrel in which the substance was put in the distillery, the proprietors of which were manufacturers of burning fluid.

The oil was obtained from the rectification of spirits made partly from rye and partly from maize. It was neutral to test-paper, of limpid colourless appearance like alcohol, and of strong fusel smell.

* The acids marked thus (?) were not procured in sufficient quantity to obtain more than probably true analytical results.

The volume was not much diminished by agitation with water, but the water when distilled gave alcohol. When distilled with a platinum wire, the thermometer rose gradually from 92° C. to 226°, at which temperature there remained a small portion of dark-coloured oil. At first water and oil came over, and then oil alone. A considerable portion had passed over before the thermometer indicated the boiling-point of amylic alcohol; but by successive rectifications, removing the water, the great bulk of the liquid had the boiling-point of 132°.

The following are the proportions of distillate for such a first distillation:—

Boiling-point.	Fluid ounces.
92°– 99° (2 layers)	4½
99°–109° (2 layers)	4½
109°–121°	3¼
121°–130°	4½
130°–134°	16
134°–136°	4½
136°–137°	4½
137°–147°	1¾
147°–168°	2
168°–200° (yellowish).....	½
200°–226° (yellowish).....	½

There remained in the retort about ¾ oz. of a reddish-brown liquid. When an alcoholic solution of caustic potash was added to the members of this series, a bright yellow colour was developed, which was deeper the higher the boiling-point. After standing for some time, the liquids were shaken with water, which was separated. They were then distilled, and the residue, which was dark and strongly alkaline, was washed several times with water; other portions of the fusel-oil were distilled from aqueous and alcoholic solutions of potash, and the alkaline liquids containing the fatty acids were united.

Examination of the Potash Solution for Fatty Acids.—The potash solutions obtained by uniting the alcoholic and aqueous solutions of potash, were evaporated to dryness after several additions of water to expel the alcohol. They were then dissolved in water and decomposed in a retort by dilute sulphuric acid, and distilled (with the addition of water) until it was supposed the fatty acids had passed over. The thumping of the retort, as the sulphate of potash separated on concentration, was avoided partly by removing the crystals, and partly by using a ring gas-burner made from a tube, and by which means the upper portion of the retort could be heated, while the bottom was kept in sand. A small portion of dark matter was left with the crystals and residue in the retort. This was tested for fatty acids (after neutralizing the free acid and separating the sulphate of potash by alcohol) by nitrate of silver; a very small quantity of whitish-brown precipitate was obtained, which did not crystallize from boiling water.

The distillate containing the volatile fatty acids consisted of an

acid aqueous fluid, upon which floated drops of dark-coloured acid oil, of a peculiar rancid smell. A small portion of the aqueous fluid was neutralized by carbonate of soda, added to the rest and distilled; nitrate of silver, added to the solution of the residue in the retort, caused a white precipitate, which immediately blackened on heating the test-tube, indicating the presence of *formic acid.* The whole of the distillate was neutralized by carbonate of soda, and evaporated *in vacuo*; it crystallized in needles like acetate of soda. As the quantity was too small for an analysis, it was heated with sulphuric acid and alcohol in a test-tube; the smell of acetic æther was distinct.

The fatty acids arising from decomposing the different potash solutions were together in such small quantities (although $1\frac{1}{2}$ gallon of fusel oil was employed), that they were united. About $\frac{1}{6}$th was neutralized by NaO CO^2, added to the whole, and distilled. Another portion of the distillate, resulting from this experiment, was treated in the same manner, and finally the whole. The soda salts thus resulting I call 1, 2 and 3; they were not in large quantity. A drop of the solution of each, evaporated upon a glass plate, was examined with the microscope.

No. 1 appeared in fibrous crystals, converging towards the centre of the drop.

No. 2 appeared to consist of two different kinds of crystals, especially as seen by polarized light; one kind in one position of the plane of blue plumose crystals, and the other of white stellated prisms.

No. 3, evaporated at ordinary temperature, appeared in feathery stellated crystals.

In neutralizing the remainder of the liquid to prepare the salt No. 3, as the fluid was approaching saturation, a peculiar motion was observed in the oil-globules floating on the surface of the liquid; they were spasmodically agitated and repelled each other, moving quickly from side to side, very much as some animalculæ appear in the field of the microscope. It was not a rotation, or movement like that of camphor, or the butyrate of baryta on water, though doubtless proceeding from the same cause.

Fatty Acids in Nos. 1, 2 and 3.—The soda salt No. 1, the residue in the retort after the first neutralization by carbonate of soda, was dissolved in water, and nitrate of silver added; the precipitate was very slight; the solution concentrated in the water-bath darkened very much. The residue after evaporation yielded to boiling water a small quantity of precipitate, insufficient for analysis, which separated on cooling. After evaporation once more *in vacuo* over sulphuric acid, the residue evolved a strong smell of acetic acid when treated with sulphuric acid, and gave with sulphuric acid and alcohol acetic æther.

The soda salt No. 2, dried up over sulphuric acid *in vacuo* to a gummy mass. On the addition of nitrate of silver to the solution, an abundant white precipitate fell, which was separated and redissolved in boiling water, from which the greater part was deposited

on cooling. The remainder yielded but little to boiling water. I obtained enough of this precipitate to make two atomic weight determinations. It burned quietly, and left a spongy mass of metallic silver, which left no residue on treatment with nitric acid. 0·11775 grm. of the salt gave 0·051 silver; and 0·128 gave 0·0555 silver, corresponding to a per-centage of silver 43·26 and 43·35. Caprylate of silver requires by calculation 43·028. I had not sufficient of this salt for an organic analysis.

Soda salt No. 3, which was slightly alkaline, was neutralized by nitric acid. The precipitate by nitrate of silver darkened slightly on boiling with water, with deposition of a small quantity of dark metallic silver on the capsule. A white curdy precipitate separated from the filtrate before cooling; and on cooling, a further quantity of a slightly grayish precipitate. This latter precipitate, which, dried at 100° C., weighed 0·0335, gave on ignition 0·016 Ag, or a per-centage of 47·74. The silver salt of œnanthic acid contains 47·161 per cent. of silver.

The white precipitate, which deposited before cooling, was dried at 100°, and was very electric; it gave the following analytical results:—0·12 grm. yielded 0·052 metallic silver, or 43·33 per cent., which agrees with caprylate of silver. I performed the organic analysis by combustion with oxide of copper. The results do not accord so well for caprylate of silver, the quantity at my disposal being almost too small for an accurate analysis of this salt; 0·1875 grm. gave CO^2=0·25575, and HO=0·1115, or a per-centage as follows:—

Carbon	37·20	16 =	96	38·20
Hydrogen	6·60	15	15	6·00
Oxygen	12·87	4	32	12·77
Silver	43·33	1	108	43·03

The filtrate from the first of these precipitations gave on evaporation in the water-bath a residue, which yielded to a little boiling water a grayish salt, which precipitated on cooling. 0·027 of this gave 0·013, or 48·14 per cent. of silver. This would correspond to caproate of silver, which contains 48·43 Ag. The residue of oil of a portion of the fusel-oil from which the above-mentioned acids were separated was treated with an additional portion of potash, and the fatty salts separated from these aqueous solutions by chloride of sodium, and decomposed in a retort by sulphuric acid. The acids were boiled with baryta water, and filtered hot; a dark resinous substance was left on the filter. On cooling, a white flaky precipitate fell; carbonic acid, passed through the filtrate from this precipitate, yielded a carbonate of baryta, from which scarcely anything could be obtained either by boiling water*, or by exhausting when dry with absolute alcohol.

The baryta salts of the fatty acids were in such small quantity that a separation and purification by crystallization was out of the

* The boiling water gave on cooling 0·445 white precipitate, which contained 34·06 per cent. BaO.

question. They appear to consist of caprate and caprylate of baryta. This solution was evaporated in the water-bath, removing the salt as soon as enough had separated to perform an atomic weight determination. The following is the result, premising that—

Œnanthylic acid requires BaO per cent. . . . . =38·44
Caprylic acid requires BaO per cent. . . . . =36·20
Capric acid requires BaO per cent. . . . . =31·94

The first salt that separated was in white, imperfectly-crystalline scales; 0·131 gave 0·0555 BaO CO^2, corresponding to 32·9 per cent. of baryta. In these crystallizations, the salt separated as a film on the surface of the liquid. The next salt, 0·53, gave BaO CO^2=0·252, or BaO per cent.=36·92. The last crystallization gave 0·194 grm. of a salt, which yielded 0·091 carbonate baryta, or 36·43 per cent. of baryta.

Examination of the Alcohols of Fusel-Oil.—The portion of fusel-oil from which the fatty acids had been separated was washed with water, and submitted to a fractional distillation. At first oil came over together with an under layer of water, which was removed, and the different products of distillation dehydrated with carbonate of potash and with fused chloride of calcium. A considerable portion of chloride of calcium was taken in solution by that portion passing over between 87° and 100°, and which crystallized out on cooling, and, after standing, in prisms or lengthened tables, similar to the compound of chloride of calcium and water. As these crystals had a peculiar smell, from which they could not be freed by pressure between blotting-paper or by exposure to the air, and as they seemed less deliquescent than the ordinary crystallized salt with water, they were fused to determine the amount of volatile matter, in order to ascertain whether perhaps they were not a compound of amylic alcohol and chloride of calcium. The loss was 49·78 per cent., which corresponds to the chloride crystallized with 6 equivs. of water, or 49·28 per cent.

After having dehydrated the portions collected between 81°–110°, 110°–132°, and 132°–136°, which last contained the great bulk of the oil, they were submitted to four rectifications, in which the following stadia were observed:—

81°–84°–90°–100°–110°–120°–129°–132°–136° C.

The residue above 136° was not sufficient to cover the thermometer. In the second rectification, 81°–84° was collected at 81°–82°–84°.

During the fourth rectification, the thermometer still continued to rise from 81°–136°, but nearly the whole of the oil was collected at 132°–136°, and the thermometer was longer stationary between 81°–84° than at any intermediate stadium. They all, where not masked by the odour of the fusel-oil (as in the case of the higher ones), smelled strongly of turpentine. The distillate between 81°–84° was rectified, and what passed over at 81° collected. Its density at 19° was 0·8194; and it presented the characteristic of alcohol contaminated with some foreign substance. After having stood for

a day over freshly ignited charcoal, water was added, in which it nearly all dissolved, giving a milky fluid, from which a little oil separated. Water was now shaken with the several distillates up to 81°–119° inclusive. The quantity of distillate was very much reduced by the water, and the resulting oil smelt strongly of turpentine. These oils, separated from the aqueous solution, stood over night upon charcoal, and were kept boiling for some time over fused chloride of calcium, so that the vapours flowed back into the flask; they were then distilled in a wax-bath from the salt. The quantity of oil thus obtained was quite small. The chloride of calcium, when dissolved in water, set free a small quantity of oil of turpentine which was mechanically mixed with it.

Since the portion of oils passing at 120°–129° was the greatest in quantity after those already mentioned, I was desirous of forming the double sulphate, in order to ascertain by that means the presence of another alcohol besides amylic. I had three-fourths of a fluid ounce at my disposal, to which was added gradually an equal weight of oil of vitriol. After having stood for a few hours, there were two layers on the addition of water; the upper one a yellowish-green oil, which diminished on the addition of more water. What remained undissolved was in too small quantity for further examination; when rectified over carbonate of potash, it began to boil at 115°, the boiling-point at once rising. When suffered to evaporate upon the hand, it smelt of amylic alcohol and turpentine. The compound sulphuric acid thus formed was neutralized by pure carbonate of baryta, and the baryta salt, after evaporation to dryness in a water-bath, was redissolved, filtered, and evaporated to crystallization. On cooling, crystals were obtained, which, under the microscope, and especially by polarized light, appeared as thin rhombic plates very much broken. I could not detect two different kinds of crystals. When dried for fifty hours *in vacuo* over sulphuric acid, these crystals presented the appearance of pearly scales, fatty to the touch. The mother-waters gave a similar salt, and the mother-water from these gave a small quantity of cauliflower-like crystals of the same appearance under the microscope: after having been dried *in vacuo*, the crystals blackened, and were decomposed when heated to 100° C.

The following is the amount of sulphate of baryta they contain, determined by incineration. They were difficult to burn; and after ignition, they were moistened with a drop of sulphuric acid, and ignited a second time:—

0·6105 gave $BaO\,SO^3$ = 0·30325 = 49·67 per cent.
0·58525 gave $BaO\,SO^3$ = 0·2895 = 49·47 per cent.

Anhydrous sulphoamylate of baryta contains 49·49 per cent. of sulphate of baryta.

Towards the close of this investigation I met with Wurtz's paper on the occurrence of butylic alcohol in a fusel-oil examined by him. I was therefore desirous of looking for this body in the fusel-oil under examination. The oils left by adding water to the product,

81°–119°, after having been treated as described above, were in small quantity, and contained fusel-oil and oil of turpentine, besides a little water. They began to boil at 105°, and were separated in two portions,—those passing between 106°–110°, and those above 110°. These two portions were treated with sulphuric acid, and the baryta salts formed. Of these, only the liquid passing at 106°–110° yielded enough for analysis, which was rendered uncertain by having unfortunately used for neutralization native carbonate of baryta which contained lime, and which was only discovered on examining the salts under the microscope, when the crystals of sulphate of lime were detected. The solutions were then evaporated to dryness, and exhausted with alcohol. The salts proceeding from the distillate above 110° yielded a small quantity of confusedly-crystallized granules, not sufficient in quantity for analysis. The remaining portion gave a salt appearing in lanceolate crystals under the microscope. The following is the analysis of the salt:—

First Crystallization.—0·184 gave 0·07875 BaO SO^3=43·21 per cent.

Second Crystallization.—The mother-waters yielded on concentration 0·14675 of a salt which contained 0·06875 BaO SO^3=47·02 per cent.

Both of these sulphates of baryta contained a small portion of sulphate of lime. The following is the quantity of fixed sulphate in three of the vinic acids:—

Sulphovinate	Lime Baryta	Sulphate	46·89 60·23
Sulphoamylate	Lime Baryta	Sulphate	36·36 49·49
Sulphobutylate	Lime Baryta	Sulphate	39·31 52·62

It appears most probable that the salts analysed were sulphoamylate of baryta with a little lime, and possibly mingled with sulphovinates. I have not therefore been able to detect Wurtz's alcohol in the specimen of fusel-oil from maize and rye. Different specimens of fusel-oil appear to vary in the nature and quantity of their constituents. The specimen examined by me contains but a very small quantity of the fatty acids.—*Journal of the Franklin Institute.*

Experiments on the Production of Urea. By Prof. Bischoff.

I. There is no doubt that urea, under all circumstances, is a product of the act of nutrition and of the exchange of the azotized substances which takes place in the organs. It is never produced by a direct transformation of albumen in the blood. The only case in which it could be developed there, would be when gelatine came to be mixed with the blood, which in the ordinary circumstances of life would never happen; otherwise it is always a product of the transformation of the solid parts of the body.

II. The quantity and quality of food, however, exercises a much greater influence than has hitherto been supposed, not only upon the transformation of the substances, but also upon the production of urea. It is true that urea is formed and secreted during complete abstinence, but the quantity greatly depends on the richness of the food in nitrogen; a dog furnished 190 grms. of urea in twenty-four hours, during which he had eaten 4 kilogrms. of meat without fat or bone, whilst the quantity of urea was reduced to 6 or 8 grms. in the same period when he had only eaten 500 grms. of potatoes and 150 grms. of fat. Non-azotized food, such as fat, always diminishes the transformation of the azotized substances. The quantity of urea also decreases; this, however, is subject to certain exceptions.

Alimentation with fat, either by itself or accompanied by a good deal of meat, produces this double effect. If the quantity of meat be only sufficient to keep up the weight of the animal, the fat diminishes the transformation in the organs, without however inducing a diminution in the urea; the quantity of which, on the contrary, may exceed that obtained with the same quantity of meat without the addition of the fat. We shall return to the cause of this result.

III. It results from other experiments, that the alimentary or organic nitrogen, exchanged in a given time, never reappears entirely as urea; but that a certain quantity, which may according to circumstances be considerable, is always eliminated in other forms.

The same thing occurs with our dog, although his urine contains no uric acid and scarcely any traces of other nitrogenous organic substances. A very small quantity of nitrogen only is rejected with the fæcal matters; and it is difficult, in fact, to ascertain the form under which the rest of the nitrogen which results from the conversion of the organic matters is eliminated, as, according to the excellent observations of MM. Regnault and Reiset, both the lungs and the skin take only a very small part in this work of secretion. It is most probable that this loss arises from a partial decomposition of the urea in the blood itself, or perhaps also in the bladder; carbonate of ammonia would be formed, which is then expelled either by the skin and lungs or with the urine.

The observations of Regnault and Reiset certainly merit all confidence, but it seems to me that hitherto they have not been carried on long enough nor with the variations of food necessary to render certain this elimination of carbonate of ammonia by the lungs and skin. Its presence in urine, on the other hand, becomes at least very probable, when this, when quite fresh, is found to be alkaline and effervescent on the addition of an acid, the animal being fasting or nourished exclusively on meat.

This quantity of nitrogen, which does not appear in the urea, remains nearly the same, notwithstanding changes in the food and the replacement of substance in the organs. Insufficient azotized nourishment (250 grms. of meat) brought it to the maximum; it then rose to two-thirds of the total quantity, whilst with 1500 grms.

of meat, which was sufficient to maintain the weight of the dog, it fell to one-third. Excess of meat caused an absolute diminution, so great that the quantity was scarcely noticeable. To me this is the best proof that the *primitive* product of the exchange of azotized matters is *urea*. A part of this urea is afterwards decomposed, and becomes, for instance, carbonate of ammonia, the quantity of which is in an inverse ratio to that of the urea. Fat appears, under certain circumstances, to resist this final decomposition; and this is why, when the food is composed of meat and fat, the quantity of urea may become greater than when it consists of pure meat, notwithstanding the property possessed by fat of moderating the exchange of azotized substances in the organs, and consequently diminishing the development of urea, because the urea formed undergoes no other changes. I believe the reason of this may be found in the relation of fat with respiration.

Lastly, water also influences this loss of nitrogen, for—

IV. The quantities of water and nitrogen in the urine always maintain very exact proportions. Amongst all its ingredients, it is the urea which has most influence upon the specific gravity of urine; the more urea there is, the greater the specific gravity. Nevertheless the total quantity of urea secreted in a given time is in intimate connexion with the quantity of water secreted in the same time; for an abundant secretion of urine, whatever may be the diminution in its specific gravity, bears with it a larger quantity of urea in a given time than a more sparing secretion.

This influence of water may depend upon many things. Water facilitates the solution of the urea and its extraction from the organs; it is even possible that it may facilitate its formation. In every case, the rapidity of the mixture depending on a larger or smaller quantity of water, this must influence the elimination of the urea. Now the secretion and excretion of urine proceeding much more rapidly in the presence of plenty of water, there remains scarcely any time for the ulterior transformation of the urea, and consequently the urine becomes richer in that substance, whilst the quantity of nitrogen derived from the parts of the organism which does not go to the formation of urea becomes so much smaller. And this is exactly the reason why a large quantity of nitrogen is lost to the urea when nitrogenous food is given in small quantities, whilst large quantities only cause a slight loss; for during complete abstinence, the quantity of urine often falls to a few cubic centimetres in several days, whilst abundant food raises it to 1200 or 1500 cub. centims. in twenty-four hours.

It is true, from what has just been said, that the quantity of urea secreted under certain circumstances and in a given time cannot be regarded as the direct register of the replacement of the nitrogenous organic substances, even when the urine contains no other body. Nevertheless urea must play the most important part in the interpretation of this vital function; it is only necessary to study the conditions of its formation and secretion better.—*Comptes Rendus*, May 16, 1853, p. 875.

On the Isomeric Combinations of Sulphur and Antimony. *By* H. Rose.

Fuchs has stated, that by the rapid cooling of fused, crystallized, black sulphuret of antimony, a modification of this substance, in the form of an amorphous reddish-brown powder, is obtained. It does not always happen that it is obtained with these properties. We more frequently get mixtures of both modifications, the grains of which give a streak, partly red and partly black, on unglazed white porcelain.

The red sulphuret of antimony has a lower specific gravity than the black; under the microscope it appears perfectly amorphous; it is harder than the crystallized black modification, and scratches not only that substance, but even calc-spar. It is also a non-conconductor of electricity, whilst the black sulphuret is a conductor.

The red modification can be very readily converted into the black. This is effected by a slight elevation of temperature, which need not go near the point of fusion, and may be about 392° F. By this means the powder becomes black, and appears crystalline under the microscope; it becomes a conductor of electricity, and acquires a higher specific gravity, which is proper to the black sulphuret. The conversion of the red into the black modification is also effected by the action of acids, especially of muriatic acid, which produces this change even in the cold, but with more rapidity with the aid of heat. Concentrated sulphuric acid does not produce a similar effect. The red powder, when boiled with muriatic acid, becomes black more quickly in proportion as the acid is less diluted. In this case a certain quantity of the sulphuret of antimony is always dissolved. Acids, which cannot decompose a small quantity of the sulphuret of antimony even by long boiling, are incapable of converting the red modification into the black. Of this class are tartaric acid or tartar and water. Dilute sulphuric acid, on the other hand, produces this change by long boiling, but more imperfectly and with much more difficulty than dilute muriatic acid.

The orange-red sulphuret of antimony, which is obtained from solutions of oxide of antimony by means of sulphuretted hydrogen, contains a very small quantity of water. This is not driven off by exposure to a temperature of 374° F., at which this sulphuret still retains its colour. At 392° F., however, it loses its water, becomes black, appears crystalline under the microscope, and becomes a conductor of electricity, whilst before heating it was amorphous and a non-conductor. This red sulphuret of antimony is also converted into the black modification by the action of acids, especially of muriatic acid; this effect, however, takes place with rather more difficulty than with the red sulphuret of antimony obtained by the rapid cooling of the black modification. This change is not produced by tartar or tartaric acid, even when the sulphuret is long boiled with solutions of these substances. The specific gravity of the sulphuret obtained with sulphuretted hydrogen is somewhat greater than that of the other red sulphuret of antimony.—*Bericht der Akad. der Wiss. zu Berlin*, 1853, p. 242.

On the Acids contained in Fungi. *By* P. Bolley.

The juice expressed from fresh Fungi has an acid reaction. Braconnot has described two acids obtained from Fungi as boletic and fungic or agaricic acid.

The author has investigated the *Clavaria flava* and the *Agaricus piperatus* and *muscarius*. He expressed the *Clavaria*, and evaporated the fluid nearly to dryness. Water was poured over the extract, and the whole allowed to stand in a glass vessel closed with bladder. In the course of a few weeks, crystals of mannite had formed in the brown mass, from which they could be mechanically separated.

The author then dissolved the extract in water, and precipitated the solution with alcohol, by which slimy matters are separated; the acid filtrate was then precipitated with solution of acetate of lead, and the lead precipitate, after washing, decomposed by sulphuretted hydrogen. The fluid contained *oxalic acid*.

In the *Agaricus piperatus*, the author, like Knop and Schnedermann, found mannite in considerable quantity. The lead precipitate, obtained in the same manner as with the preceding fungus, contained a different acid, which appeared to be fumaric acid. Its analysis gave—

Carbon	41·84	8	41·38
Hydrogen.....	3·52	4	3·45
Oxygen	54·64	8	55·17

By a comparison of the statements published by Braconnot and others regarding boletic acid, the author comes to the conclusion that boletic acid is nothing but fumaric acid.

Agaricus muscarius also furnished an acid fluid, but the acid could not be prepared in sufficient quantity; oxalic acid, however, was not present. The extract, when alcohol was poured over it, became tolerably fluid and nearly clear; it was filtered, and the filtrate, when water was added to it, exhibited a considerable milky turbidity, which was increased by further addition of water. It was then filtered, and the filter, to which the white flakes adhered, extracted with hot alcohol; the addition of water to the fluid reproduced the white turbidity; it had a strong acid reaction, and when allowed to stand without addition, furnished, as the alcohol evaporated, small cauliflower-like groups of acid crystals of a strong rancid taste. These crystals were readily soluble in alcohol and æther. The quantity obtained was insufficient for an elementary analysis. Heated with strong ammonia, the acid was dissolved; a gelatinous mass separated on the cooling of the solution. The author prepared the soda salt by boiling the acid with carbonate of soda, evaporating, and dissolving in absolute alcohol; from this solution he obtained the silver salt by the addition of nitrate of silver, which produced a dirty white precipitate, of an unpleasant odour, which becomes bluish in the light, and fuses when heated. This behaviour of the soda and silver salts agrees with the statements of Schnedermann

and Knop* respecting lichestearic acid, to which the acid found by the author exhibits a great resemblance in its physical properties.

This opinion is further supported by the fact, that Pfaff found fumaric acid in Iceland moss, and that Schnedermann and Knop discovered the lichestearic acid in the same lichen. It may therefore readily be supposed that these two acids may coexist in Fungi.

The author has referred particularly to L. Gmelin's supposition, that the fungic or agaricic acid may be malic acid; he did not succeed, however, in finding malic acid in the fungi investigated by him.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 44.

On the Conversion of Tartaric Acid into Racemic Acid. By M. Pasteur.

I have succeeded in converting ordinary tartaric acid into racemic acid, completely identical in all its chemical and physical properties with natural racemic acid. Like this, it splits, under the same circumstances, into dextro- and lævotartaric acid, showing equal rotatory powers in opposite directions in their combinations with bases.

In the different preparations which I have made, I have always ascertained, by the most delicate tests, that the tartaric acid which I employed contained no natural racemic acid.—*Comptes Rendus*, June 6, 1853, p. 973.

Investigation of Stanmethyle, a new Organic Radical containing Tin. By Auguste Cahours *and* Alfred Riche.

In a paper presented to the Academy of Sciences†, we have already shown that the action of metallic tin upon hydriodic æther in closed vessels at a temperature of about 320° F., produces a great abundance of the iodide of a ternary radical, $C^4 H^5 Sn$, to which we gave the name of *stanæthyle*.

The substitution of iodide of methyle for iodide of æthyle gave exactly similar results. When tin acts upon iodide of methyle at a temperature of from 302°–356° F., the latter is completely decomposed in the course of fifteen to twenty hours, and on cooling the liquid forms a solid mass. This, submitted to distillation, gives a limpid liquid, of a strong odour; it begins to boil at 383° F., and the distillation ends between 428° and 437° F. The last portion, which boils at 428° F., and which constitutes at least three-fourths of the crude substance, forms a crystalline mass on cooling; that which boils at about 392° F. remains fluid even at 32° F.

If the solid mass be again fused and left to cool slowly, the crust formed on the surface pierced, and the internal fluid rapidly decanted, magnificent crystals of an oblique, rhomboidal, prismatic form are obtained. This compound fuses at 84° F. It is tolerably soluble in water, more so in alcohol, and dissolves in æther in almost any proportions. Its solubility in these fluids is much greater than that of the corresponding compound, iodide of stanæthyle.

When ammonia is poured into the watery solution of this body, a white amorphous precipitate is obtained; this is soluble in an ex-

* Chem. Gaz., vol. iv. p. 54. † *Ibid.*, vol. x. p. 307.

cess of potash, but insoluble in an excess of ammonia, in alcohol and æther. This oxide, like the oxide of stanæthyle, resembles oxide of tin in these respects. It only differs from the preceding compound in having changed 1 atom of iodine for 1 of oxygen.

Oxide of stanmethyle dissolves rapidly in sulphuric, nitric, muriatic, hydrobromic, formic and acetic acids, forming fine crystalline compounds; the sulphate and nitrate may also be obtained from the watery solution of the iodide by means of sulphate and nitrate of silver; the oxide would also be formed by boiling the iodide with oxide of silver.

We have analysed the chloride, C^2H^3Sn,Cl, bromide, C^2H^3Sn,Br, iodide, C^2H^3Sn,I, sulphate, C^2H^3Sn,O,SO^3, nitrate, C^2H^3SnO,NO^5, carbonate, C^2H^3SnO,CO^2, oxalate, C^2H^3SnO,C^2O^3, and acetate, $C^2H^3SnO,C^4H^3O^3$, of stanmethyle; the results of the analyses may be represented by the above formulæ.

In the series of stanæthyle we have obtained some new combinations, such as the carbonate, oxalate and phosphate, which are insoluble; the acetate, tartrate and formiate, which are rather soluble in water, and crystallize perfectly; the sulphuret, which is produced by pouring solution of sulphuretted hydrogen into the iodide, or by passing through the latter a current of sulphuretted hydrogen gas; the sulphuret is deposited in limpid drops, which are insoluble in water, but soluble in alcohol. They solidify very slowly, and both in the solid and liquid state have the composition of sulphuret of stanæthyle.

These substances possess a corresponding composition to those which we have obtained in the methylic series. Thus representing stanmethyle by SnMe, and stanæthyle by SnAe, we get two series offering the most perfect parallelism:—

SnMe .....stanmethyle.	SnAe.....stanæthyle.
SnMe, I .....iodide of stanmethyle.	SnAe, I.....iodide of stanæthyle.
SnMe, Cl .....chloride of stanmethyle.	SnAe, Cl .....chloride of stanæthyle.
SnMe, Br .....bromide of stanmethyle.	SnAe, Br .....bromide of stanæthyle.
SnMe, S .....sulphuret of stanmethyle.	SnAe, S.....sulphuret of stanæthyle.
SnMe, O.....oxide of stanmethyle.	SnAe, O.....oxide of stanæthyle.
$SnMeO,NO^5$ ...nitrate of stanmethyle.	$SnAeO,NO^5$ ...nitrate of stanæthyle.
$SnMeO,SO^3$ ...sulphate of stanmethyle.	$SnAeO,SO^3$ ...sulphate of stanæthyle.
$SnMeO,C^2O^3$...oxalate of stanmethyle.	$SnAeO,C^2O^3$...oxalate of stanæthyle.

The liquid product formed at the same time as the iodide of stanmethyle, and which boils about 392° F., is the iodide of a new radical, which must contain 2 atoms of stanmethyle condensed into 1. This iodide possesses a penetrating odour, less powerful however than that of the corresponding compound obtained during the action of tin upon iodide of æthyle. It is decomposed by ammonia, giving an oxide which forms crystallizable compounds with acids.

During the action of tin upon iodide of æthyle, a small quantity of an oil, possessing an odour of horse-radish, is formed; it is produced in great quantity when the action is stopped at the end of a few hours. This is the iodide of a radical $(SnAe)^2$, I, corresponding

with the iodide $(SnMe)^2, I$; treated with ammonia, it gives an amorphous oxide, which produces crystallizable salts.

By substituting phosphuret of tin for the metal, we obtain, besides the iodide of stanæthyle and the compound $(SnAe)^2, I$, a liquid iodide, which like the preceding was procured by Löwig by the action of the alloy of sodium and tin upon iodide of æthyle.

Arsenic acts upon hydriodic and methylhydriodic æther, producing compounds analogous to stibæthyle and stibmethyle, which take fire in the air when slightly heated, and diffuse an insupportable odour of garlic.

Arseniuret of zinc is rapidly attacked by iodide of æthyle, furnishing a white crystalline substance, represented by the formula—

$$C^{12} H^{15} As, I + C^4 H^5 ZnI.$$

Arseniuret of potassium becomes heated in contact with iodide of æthyle; the latter immediately begins to boil, and furnishes products which inflame with the greatest facility.

Lead, contrary to the assertion of Dr. Frankland, is readily attacked, whilst copper, with its arseniuret and phosphuret, does not appear to produce any action with iodide of æthyle.

Tin, therefore, with æthyle and methyle, forms radicals, which play the part of true compound metals, and furnish perfectly concordant series of salts.

Iodide of amyle is not decomposed by tin at 356° F.; if the temperature be raised to 428°–464° F., it quickly acts upon the metal, and furnishes products which will form the subject of another communication.—*Comptes Rendus*, June 6, 1853, p. 1001.

ANALYTICAL CHEMISTRY.

On the Estimation of Iron, Cyanogen, Hydrocyanic Acid, and Hydrosulphocyanic Acid by Volume Analysis; and on the Quantitative Determination of the Sulphocyanide of Potassium in Saliva. *By* THORNTON J. HERAPATH, *Assistant Lecturer on Practical Chemistry in the Bristol School of Medicine, &c. &c.**

A FEW months ago, I described a process by which small quantities of iron might be easily and accurately estimated by means of a colorimeter†, and pointed out its value in the analysis of waters, where the chemist is often called upon to estimate with exactness exceedingly minute quantities of that metal or its oxides. I have since discovered that the same process is applicable in many other cases, and may be resorted to with advantage for the estimation of the peroxide of iron contained in the ashes of plants and animal matters, as well as in the analysis of guanos and other manures, and even in the determination of the atomic weight of some ferruginous com-

* Communicated by the Author.

† Quart. Journ. of Chem. Soc., April 1852; also Chemical Gazette, May 1st, 1852.

pounds, when the operator has but a small quantity of the material at his disposal. To the former purpose, indeed, it appears to be particularly well adapted; and by taking advantage of this circumstance, the agricultural chemist may often effect a great saving of time and labour—considerations of no mean importance, as I need hardly observe, in ordinary commercial analyses, where the experimentalist is often allowed but a few hours to perform the analysis of the manure and report upon its value. The same process, also, I find, by introducing one or two simple modifications, may be employed as a means of estimating quantitatively cyanogen, hydrocyanic acid or prussic acid, and hydrosulphocyanic acid.

1. *On the Estimation of Oxide of Iron in the Ashes of Plants and Manures, &c.*

The mode in which I operate is as follows:—

The ash, or other substance to be subjected to analysis, is acted upon with boiling muriatic acid, and the mixture evaporated to dryness in the usual manner. The dried mass thus obtained is then again treated with a small quantity of strong hydrochloric acid, and the whole is heated over a gas-jet until everything soluble in that menstruum is dissolved. It is afterwards diluted with water and thrown on a filter, in order to separate the silica. The acid solution which passes through the filter is next heated to the boiling-point with the addition of a few drops of nitric acid, and supersaturated with ammonia, which precipitates the iron as peroxide, either pure or combined with phosphoric acid, and more or less contaminated by the phosphates of lime and magnesia. The precipitate having been collected on a filter, washed, dried, and weighed in the usual manner, it is redissolved in boiling hydrochloric acid, and the solution introduced into a graduated burette, the scale of which is divided into 100 parts. Five, ten, or twenty measures of the solution are then taken, and poured into the colorimeter; an excess of sulphocyanide of potassium is added, and the mixture diluted with water to the necessary degree, that is to say until it occupies 500, 1000, 10,000, or 20,000 water grain-measures. The tint is then compared with that produced by the gradual addition of a standard solution of iron of known strength to the water impregnated with sulphocyanide of potassium, which is contained in another colorimeter of similar dimensions, placed side by side with the one before alluded to on a sheet of white writing-paper. From the number of measures of the ferruginous solution that are required in order to render the fluids in the two instruments uniform in tint, the proportion of iron in the solution operated upon is ascertained. For example, the phosphatic precipitate obtained from the ash of 20 grs. of a guano was redissolved in acid, and the solution diluted with water. A tenth part of this solution was introduced into a colorimeter, and tested with sulphocyanide of potassium as before described. The tint produced was found to be equal to that formed by $10\frac{1}{2}$ measures of a standard solution of iron containing $\frac{1}{10}$th part of a grain of anhydrous peroxide of iron in 100 measures. Hence

it follows that the guano contained 0·525 gr. of peroxide of iron per cent. Thus $0{\cdot}0105 \times 10 = 0{\cdot}105$, which being multiplied by 5 gives $0{\cdot}525\%$.

2. *On the Quantitative Estimation of Cyanogen and Hydrocyanic Acid.*

The process I am about to describe is founded on the reaction that was first pointed out, I believe, by Prof. Liebig *. This chemist has shown that when some sulphide of ammonium and caustic ammonia are added to an aqueous solution of prussic acid, and the mixture is heated with the addition of flowers of sulphur; or when a mixture of prussic acid and ammonia is gently heated with pentasulphide of ammonium, the hydrocyanic acid is soon converted into sulphocyanide of ammonium. The prussic acid having been obtained therefore in the form of an aqueous solution, either by simple distillation, with or without dilute sulphuric acid, or, in the case of some cyanides, by first converting the cyanogen into prussic acid by the action of nascent hydrogen, by the process described by Mr. Heisch †, it is treated with an excess of the mixture of pentasulphide of ammonium and *liquor ammoniæ*, afterwards gently heated, and carefully evaporated to dryness. The saline mass remaining is then redissolved in boiling water, and the solution filtered, and introduced into the colorimeter, where it is treated with a slight excess of perchloride of iron. The tint produced is then compared from time to time with that of the liquid in another colorimeter containing a weak solution of perchloride of iron, to which a standard solution of sulphocyanide of ammonium or sulphocyanide of potassium is gradually added until the two correspond. From the number of measures of the sulphocyanide or test-solution that have been taken, the proportion of cyanogen or of hydrocyanic acid may be readily calculated.

This process, I find, furnishes far more correct results than can be obtained by the ordinary modes of analysis, particularly when the cyanogen compound occurs in minute quantity. By taking the proper precautions, and employing small-sized colorimeters, the $\frac{1}{3000}$dth of a grain of hydrocyanic acid may be estimated with the greatest exactness.

3. *On the Quantitative Estimation of the Sulphocyanide of Potassium in Saliva.*

Great differences exist in the determinations that have been made of the proportion of sulphocyanide of potassium in human saliva. According to Jacubowitsch ‡, it amounts to $0{\cdot}006\%$; whilst Lehmann § estimates it at from 0·0046 to $0{\cdot}0089\%$; and Wright ‖ places it so high as 0·51 to $0{\cdot}98\%$. The cause of these discrepancies evidently originates in the difficulty that has been hitherto experienced in

* Chem. Gaz., 1847, p. 143.
† Quart. Journ. of Chem. Soc., vol. ii. p. 219.
‡ De Salivo et Muco; dissert. inaug. Amstelod. 1849.
§ Physiological Chemistry (English edition), vol. ii. p. 20.
‖ On the Physiology and Pathology of the Saliva. Lancet, 1842.

estimating small quantities of sulphocyanogen with any great degree of accuracy.

By adopting my process, however, this obstacle is removed; and hence I determined to subject the matter to a fresh investigation.

Specimens of saliva were therefore collected from different individuals, and tested in the following manner:—They were first evaporated to dryness in a water-bath or a gas-oven, and the residue was acted upon with dilute hydrochloric acid. The solution having been filtered in order to remove any albuminous or mucoid flocculi that were suspended in it, was poured into a colorimeter, where it was diluted with pure distilled water to the necessary degree, care having been taken to add previously a drop or two of a solution of perchloride of iron. The tint produced was then compared with that of a standard solution of pure sulphocyanide of ammonium, containing a known quantity of sulphocyanogen per cent., which was employed in the manner before described. The results of my experiments are subjoined:—

	Experiment	Quantity of saliva taken. grs.	Sulphocyanogen contained therein. gr.	In 10,000 parts by weight of saliva. Sulphocyanogen.	Sulphocyanide of potassium.
Saliva of a young man aged 24.	1.*	1603	0·1001	0·624	1·044
	2.	509	0·0065	0·128	0·215
	3.*	790	0·0463	0·586	0·981
	4.	400	0·0085	0·212	0·356
	5.	806	0·0277	0·344	0·575
Saliva of a young man aged 18.	1.*	2014·3	0·0967	0·480	0·803
	2.	588·2	0·0228	0·388	0·650
	3.	602·5	0·0199	0·331	0·555
Saliva of a young woman aged 28.	1.	614·2	0·0030	0·0486	0·078
	2.	650	0·0041	0·0616	0·103
	3.	395	0·0081	0·2027	0·339

Mansion House, Old Park, Bristol,
July 21st, 1853.

PROCEEDINGS OF SOCIETIES.

Royal Institution.

May 27th, 1853. (Right Hon. Baron Parke, Vice-President, in the Chair.)

"On the Formation of Hydrogen and its Homologues," by B. C. Brodie, Esq., F.R.S.

In what is termed mineral chemistry, chemical substances are classified according to the different nature of the elements of which they consist. But in organic chemistry this distinction is no longer available. Organic substances were formerly defined as triple com-

* In these experiments, the secretion of the saliva was excited by smoking tobacco.

pounds of carbon, hydrogen and oxygen; and this, with the statement of the relative proportion of these elements in any given compound, was all that was attempted to be made out as to its constitution. But this class of bodies is more numerous possibly than all the other chemical substances taken together with which we are acquainted, and some further distinction was necessary for the purposes of science. The sagacity of certain chemists at length discovered a relation which was capable of becoming the basis of a truly rational and natural classification. It was perceived, that in the long series of chemical changes of which these bodies were susceptible, the whole of the substance did not change, and that in these combinations certain *groups* of elements had the same persistent character and fulfilled the same chemical function as the simple elements themselves in other bodies. These constant groups have been named *radicals*. Among these, those hydrocarbons termed the homologues of hydrogen are of special interest. Æthyle, a group consisting of 2 atoms of carbon and 5 of hydrogen, $C^2 H^5$, is one of these bodies. Assuming water as 2 atoms of hydrogen and 1 of oxygen, HHO, alcohol is composed of 1 atom of æthyle, 1 of hydrogen, and 1 atom of oxygen, $(C^2 H^5) HO$. Hydriodic acid, the iodide of hydrogen, consists of an atom of hydrogen combined with an atom of iodine, HI. The iodide of æthyle consists of an atom of æthyle combined with an atom of iodine, $(C^2 H^5) I$. It is from these, and other like analogies between hydrogen and æthyle, that the idea arose of the similarity in their chemical function.

Certain chemists, however, conceived these views to be mere fanciful speculations. Their principal objection, reasonable or not, was that this æthyle was a purely ideal substance. From hydrochloric acid, or from water, we readily procure hydrogen. We separate metals from their combinations; but æthyle could not thus be obtained, and there was a point where it seemed that this analogy failed. Frankland however has silenced this objection in the most satisfactory manner, namely by procuring and isolating this æthyle.

He prepared it by a modification of the form of experiment by which hydrogen itself is prepared. He placed together zinc and iodide of æthyle in tubes hermetically sealed, and heated them considerably above the boiling-point of water. On opening the tubes, the æthyle escapes as a colourless combustible gas. There is only one property of æthyle on which I need dwell—its specific weight; it is about twice the weight of air.

Æthyle, however, when procured, did not realize all the anticipations formed of it, and there was one very important difference between the actual and the anticipated æthyle. It was supposed that when zinc acts upon iodide of hydrogen, it takes away (so to say) the iodine, and the hydrogen becomes what is termed *free*, and the same with æthyle. On this view, æthyle would have a certain atomic constitution, $C^2 H^5$. Now there is much reason to believe, that in the gaseous form the molecules of all bodies occupy the same space, whether this molecule consist of 2 only, or, as may be the case, of 100 atoms. Hence to ascertain of how many atoms the

molecule of a substance consists, we have simply to compare its weight in the gaseous form with that of some other gas of which the molecule is already determined. When this experiment was made with æthyle, it was found to be just twice as heavy as it should be; that is to say, the space which should have contained 2 atoms of carbon and 5 of hydrogen was found to contain just twice that quantity, or $C^4 H^{10}$.

Some chemists considered that æthyle was an exception to the general rule, and that the molecule of æthyle only occupied half the space of the molecule of other bodies, so that the same space which contained 1 molecule of water truly contained 2 molecules of æthyle. This however is evidently but an arbitrary assumption to meet the case. Others said that, after all, the true æthyle remained yet to be discovered, and that this body was not it, but a hydrocarbon isomeric with it, for that the real æthyle would have only half the density of this body.

There is however a third view, on which the æthyle of theory is also the æthyle of fact. On a former occasion, I showed reasons for believing that the elements are in a certain sense compound molecular groups, consisting of 2 or more atoms, which (in the present state of our knowledge) we must regard as similar, united to form a compound molecule. On this idea, the gas hydrogen is represented, not by the symbol H, but as HH; and æthyle, the analogue of hydrogen, would also consist of a double atom, and be represented, not as $C^2 H^5$, but as $C^2 H^5 C^2 H^5$.

The old view, however, had always a certain advantage over this, in the clear and consistent account which it gave of the mode of formation of hydrogen. How is it, it may be asked, and by what process, that this compound atom of hydrogen is formed? The answer is by no means obvious. Indeed the investigation of the nature of the process by which æthyle was formed alone gave the key to its solution.

Æthyle is not, in truth, made by the direct action of zinc upon the iodide of æthyle; but by the intervention of another body, which belongs to the class of what I may term fugitive or evanescent combinations, and which is made and decomposed again in the course of the experiment. This body is zincæthyle. The molecule of zinc, consisting of 2 atoms, ZnZn, splits into two parts. 1 atom, Zn, combines with the iodine of the iodide of æthyle, $C^2 H^5 I$, to form iodide of zinc, ZnI, while the other atom at the same moment combines with the æthyle, forming zincæthyle, $Zn\ C^2 H^5$.

The mode of action of zincæthyle upon iodide of æthyle is perfectly analogous to its action upon water. In contact with water, HHO, it immediately decomposes, forming hydrated oxide of zinc, ZnHO, and hydride of æthyle, $C^2 H^5 H$. This hydride of æthyle has hardly more than half the density of the æthyle gas. In the same space in which, in the other case, are contained 2 heavy atoms of æthyle, are here contained 1 heavy atom of æthyle and 1 light atom of hydrogen. Now the zincæthyle with the iodide of æthyle decomposes in a perfectly similar manner, forming iodide of zinc,

ZnI, and æthyle gas, $C^2 H^5 C^2 H^5$. That this is truly the mode of the formation of the æthyle is proved by the fact, that by careful modification of the experiment, it is possible to break up this process of the formation of the æthyle into the two factors (so to say) of which it consists*. At a low temperature the zincæthyle alone is formed. At a higher temperature the zincæthyle disappears, and the æthyle is produced.

It is evident that the formation of the compound molecule of hydrogen, HH, must be a very different physical event to the formation of the single atom of hydrogen, H, if such could exist. The ordinary hypothesis of the "*liberation*" of hydrogen gives us no conception of its nature: we need some other explanation.

It seems to me probable, that when zinc acts on hydrochloric acid and water, there are, as in the case of æthyle, two steps in the process,—the first, the formation of a zinchydrogen, ZnH; the second, the action of this zinchydrogen on the water, with the formation of hydrated oxide of zinc, ZnHO, and hydrogen gas, HH. There are various arguments in favour of this view. First, it explains the result, which the other hypothesis does not. Secondly, the analogy of æthyle compels us to it. It is not probable that bodies so similar in other respects are dissimilar in the mode of their formation. Thirdly, there is at least one experiment in which we are absolutely able to analyse the process of the formation of hydrogen, and to prove that it does take place in this manner.

This remarkable experiment is the formation of hydrogen by the decomposition of hypophosphorous acid by copper salts†. Hypophosphorous acid is, like zinc, what is termed a reducing agent. It precipitates certain metals from their solutions, and by a process of deoxidation decomposes alkalies with the formation of phosphorous acid and hydrogen. If this hypophosphorous acid be *boiled* with the copper salt, nothing is perceived but the formation of metallic copper and hydrogen gas; but if the solution be gradually heated, and the action arrested at a certain point, it can be shown that this formation of hydrogen is preceded by the formation of a combination of hydrogen and copper, $Cu^2 H$, analogous to zincæthyle. The part which this bears in the formation of the hydrogen is distinctly shown by the action of acids, hydrochloric acid, HCl, for example, upon it. This acid, which does not act upon metallic copper, immediately decomposes this body, forming protochloride of copper, $Cu^2 Cl$, and hydrogen, HH.

This hydride of copper has only a very ephemeral existence. It is decomposed very nearly at the same temperature at which it is produced, and its formation for this reason had long been overlooked by chemists. We can hence readily comprehend that other combinations of this class may take place in the case of which the temperature of formation and of decomposition may either coincide, or so closely approximate to each other, that it may ever be impossible to isolate the substance produced. This is probably the case in the action of zinc.

* See Quarterly Journal of the Chemical Society, vol. iii. p. 405.

† See Ann. de Chim., 3rd series, vol. xi. p. 250.

THE CHEMICAL GAZETTE.

No. CCLX.—August 15, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Upon some Bitter Principles. By F. ROCHLEDER *and* R. SCHWARZ.

IT was first observed that the wood of *Quilandina Moringa*, by extraction with hot water, furnished a fluid which appeared yellow by transmitted, but blue by reflected light. A similar property was afterwards found by Frischmann to exist in the bark of *Æsculus Hippocastanum*, and by Nolde in red sandal-wood and quassia.

After a considerable time, Raab described the principle which produced this dichroism in the above-mentioned fluids, under the name of *schillerstoff*. Martius called it *bicolorine*, Kastner *polychrome*. Raab believed that the substance was contained in the plants combined with an acid, forming a basic salt; he stated that it could be obtained pure by adding sulphate of copper, and afterwards carbonate of potash, to its concentrated watery solution, as by this means all extraneous matters were removed.

Several methods for the preparation of æsculine have been proposed by Martius, St. George, Minor, Kalkbrunner and Trommsdorff. The authors employed Minor's process, which is more simple than the others.

The finely-divided bark of the horse-chestnut is extracted with water, the expressed decoction precipitated with solution of acetate of lead, and filtered from the precipitate; sulphuretted hydrogen gas is then passed into the filtered fluid, and the sulphuret of lead separated by filtration; the clear wine-yellow fluid is then evaporated on the sand-bath to the consistence of weak syrup, and left quiet in a cool place. After several days the whole sets into a jelly of crystals, which is put upon linen and allowed to drain, so as to remove the brown mother-liquor, and then expressed under gradually increased pressure.

The residue is recrystallized three or four times from hot alcohol of spec. grav. 0·951, and a similar number of times from boiling water; the crystals last obtained are washed with cold water on the filter until about a third of them is dissolved. The undissolved portion is pure æsculine. The æsculine contained in the mother-liquors may be obtained from them by distilling off the alcohol, evaporating the water on the water-bath, and adding the residues together. The æsculine separates in crystals, which are slightly coloured.

Pure æsculine possesses a dazzling white colour; it forms prisms, which are often grouped in a globular form; it is bitter and in-

odorous. It has been stated that æsculine is not thrown down by metallic salts; the authors found that tribasic acetate of lead precipitated æsculine from its watery solution. The precipitate is of a pale yellowish colour, and is partially decomposed during washing. In other respects the authors found all Trommsdorff's statements regarding æsculine to be correct.

Æsculine was analysed by Trommsdorff, who calculated the formula $C^{16}H^{9}O^{10}$ from the results of his analyses. The authors' analyses gave numbers which agree very closely with those ascertained by Trommsdorff. Trommsdorff remarks, that it is impossible to determine the atomic weight of æsculine, as it enters into no combination which appears fit for such a purpose. The authors have endeavoured to effect this determination in a different manner; with this view, they have investigated the products of the decomposition of æsculine.

The decomposition which æsculine undergoes by the action of mineral acids appears to furnish the means of effecting this determination. If æsculine be boiled with muriatic acid or slightly-diluted sulphuric acid, humus-like products are obtained (as is the case under similar circumstances with sugar), with which a small quantity of shining crystals is mingled. If a more diluted acid be employed, and the temperature be not raised to the boiling-point, better results are obtained.

The following method was found most advisable:—As much water is poured over the æsculine as would be necessary to dissolve it at a boiling heat; the eighth part (by volume) of hydrate of sulphuric acid is then added. The dish containing this mixture is then heated on the water-bath. The æsculine is dissolved, the fluid acquires a yellow colour, and after a short time acicular crystals are deposited on the sides of the dish, which continually increase in quantity. When the fluid is so concentrated by evaporation that the sulphuric acid would effect a more extended decomposition, which may be ascertained by the colour of the fluid at the edges, the dish is taken from the water-bath, and allowed to stand for a day at a temperature of from 46°–50° F. The crystals, which have increased whilst the fluid has been standing, are separated from the acid fluid by filtration. Carbonate of lead is added to this as long as an effervescence is produced by the addition of a fresh quantity of this salt; it is then heated, and filtered from the sulphate of lead. It is of a faint greenish colour, and contains a trace of oxide of lead. Animal charcoal is added to it; it is heated to boiling, and filtered. In this manner the fluid is obtained perfectly free from lead and decolorized. When evaporated on the water-bath, it leaves behind a thick, pale yellowish syrup, of a very sweet taste, which solidifies into a mass of crystals after standing for about a fortnight.

The above-mentioned prismatic crystals must be purified from a small quantity of a brownish-yellow colouring matter which adheres to them obstinately. For this purpose they are dissolved in boiling water; animal charcoal is added to the solution, which is filtered after some time from the charcoal whilst boiling. The cry-

stals separate from the solution during its cooling. In this manner they have only a faint tint of yellow. The analysis of the substance prepared from æsculine by the action of muriatic acid, and purified in the above way, is given under I., and that of the substance prepared with sulphuric acid under II.

The crystals of this substance, to which the authors give the name of *æsculetine*, are very difficult of solution in water; even boiling water dissolves only a small quantity of them, which separates again on cooling in the form of needles and laminæ, exhibiting the closest resemblance to benzoic acid. Collected on a filter and dried, they cover the paper in the form of a silvery film, which is readily removed. Æsculetine is but sparingly soluble in cold alcohol, but dissolves readily in this fluid when boiling; the greater part of it separates again on the cooling of the solution. It possesses the characters of a very weak acid. Water containing a little alkali dissolves it readily. These solutions are of a golden-yellow colour; the colour disappears on the addition of an acid, and the æsculetine is precipitated in thin silky needles. The behaviour of æsculetine with ammonia shows that it is a very weak acid. If some æsculetine be dissolved in the smallest sufficient quantity of boiling solution of ammonia, the ammoniacal salt separates on the cooling of the solution in shining laminæ of a citron-yellow colour. If these be collected on a filter, pressed between blotting-paper, and exposed to the air for a couple of hours, the ammonia is volatilized, and unchanged æsculetine remains. The smallest quantity of an alkali or alkaline earth is sufficient to give a yellow colour to æsculetine or its solutions. If the alcohol in which it is dissolved contains a trace of lime, as is frequently the case, the æsculetine crystallizes from the solution on cooling in beautiful yellow crystals, which however scarcely leave a perceptible residue of lime after combustion.

If it be desired to free the æsculetine from every trace of the colouring matter which adheres to it so obstinately, this can only be effected by moistening it with ammonia, placing the yellow mass on a filter, and washing it with water. When a third part of the yellow mass is dissolved in the water, all the colouring matter has been removed with some æsculetine. The portion remaining on the filter is then dissolved in the necessary quantity of water, and muriatic acid added to the solution. The colourless crystals which are deposited are then filtered from the fluid, which is also colourless; whilst the first portion, which contains colouring matter as well as æsculetine, acquires a reddish or violet colour on the addition of muriatic acid. The analysis of æsculetine purified in this manner will be found under III.

When heated, æsculetine fuses, becoming brown at the same time; and if the action of heat be continued, the greater part of it is decomposed. A large cinder is left, whilst a small quantity of a sublimate, apparently consisting of æsculetine which has escaped decomposition, imbued with an empyreumatic oil, is obtained.

A watery solution of æsculetine is coloured green by chloride of

iron, without the formation of a precipitate. As æsculine dissolves with a green colour in boiling water to which chloride of iron has been added, it appears that under these circumstances æsculine is decomposed and æsculetine formed. Analyses of æsculetine, dried at 212° F., gave—

	I.	II.	III.			
Carbon	60·75	60·78	60·51	18 =	108	60·67
Hydrogen ..	3·51	3·47	3·62	6	6	3·37
Oxygen	35·74	35·75	35·87	8	64	35·96

When a boiling watery solution of æsculetine is mixed with solution of acetate of lead, a voluminous precipitate of a citron-yellow colour, as gelatinous as hydrate of alumina, is produced. This was washed with boiling water, and dried at 212° F. During drying it shrunk up, and became remarkably like gamboge. When powdered, it resembled chromate of lead. Analysis gave—

Carbon.....	27·95	108 =	648·000	28·12
Hydrogen	2·17	48	48·000	2·08
Oxygen	20·54	60	480·000	20·81
Oxide of lead	49·34	11	1129·118	48·99

$$C^{108}H^{48}O^{60}+11PbO=6(C^{18}H^{8}O^{10})+11PbO.$$

It is extremely probable that the salt was originally constituted according to the formula $C^{18}H^{8}O^{10}+2PbO$, and that it has undergone the commencement of a decomposition during the washing. The above salt may be regarded as a mixture of two lead salts produced by this means, thus—

$$5(C^{18}H^{8}O^{10}+2PbO)+(C^{18}H^{8}O^{10}+PbO).$$

After deduction of the oxide of lead, the organic substance combined with it may be calculated as follows:—

Carbon.....	55·17	18 =	108	55·10
Hydrogen	4·28	8	8	4·08
Oxygen	40·55	10	80	40·82

If this composition be compared with that of free æsculetine, it appears that in contact with oxide of lead and water it has taken up 2 equivs. of water, which are not expelled at 212° F. If an alcoholic solution of æsculetine be precipitated with an alcoholic solution of acetate of lead with heat, a powdery precipitate of a fine citron-yellow colour is obtained; this, when washed with hot alcohol, and dried at 212° F., had the following composition:—

Carbon	28·71	180 =	1080·000	29·00
Hydrogen	1·19	40	40·000	1·07
Oxygen	12·44	60	480·000	12·88
Oxide of lead....	57·66	19	2123·022	57·05

$$C^{180}H^{40}O^{60}+19PbO=10(C^{18}H^{4}O^{6})+19PbO.$$

In this case also the lead salt appears originally to have had a composition agreeing with the formula $C^{18}H^{4}O^{6}+2PbO$, but to have lost oxide of lead during the washing. After deduction of

57½ per cent. of oxide of lead, the following composition may be calculated for the organic substance:—

Carbon.....	67·55	18 =	108	67·50
Hydrogen.....	2·80	4	4	2·50
Oxygen	29·65	6	48	30·00

Here 2 equivs. of water are expelled from the æsculetine, and the formula of free æsculetine, $C^{18}H^6O^8$, must consequently be written $C^{18}H^4O^6+2HO$.

The sweet substance, mentioned above as being formed, together with æsculetine, during the action of acids upon æsculine, forms crystals which fuse at 212° F. They were dried at this temperature, and gave on analysis the following numbers:—

Carbon	37·71	12 =	72	38·09
Hydrogen	6·92	13	13	6·87
Oxygen	55·37	13	104	55·04

This sweet substance is consequently a hydrate of carbon. When dried at 212° F., it contains 1 equiv. more hydrogen and oxygen than grape-sugar dried at the same temperature. Its taste is much more intensely sweet than that of grape-sugar. When treated with a solution of oxide of copper in potash, the reduction to protoxide of copper was instantaneously effected.

The following are the results of analyses of pure æsculine. The material for each analysis was derived from a different preparation of the substance:—

Carbon.....	51·96	52·01	51·79	..	42	=252	52·07
Hydrogen	5·39	5·27	5·04	5·15	24	24	4·96
Oxygen	42·65	42·72	42·17	..	26	208	42·97

The formula of æsculine only differs from that of phloridzine in the quantity of oxygen:—$C^{42}H^{24}O^{20}$ phloridzine $+O^6=C^{42}H^{24}O^{26}$ æsculine.

If the composition of æsculine be compared with that of the æsculetine, and of the sweet substance produced by its decomposition, the following connexion results:—$C^{42}H^{24}O^{26}$ æsculine $=C^{18}H^4O^6$ æsculetine $+2(C^{12}H^{10}O^{10})$.

The assimilation of 8 equivs. of water gives $C^{18}H^4O^6+2HO$ and $2(C^{12}H^{13}O^{13})$.

Æsculetine, in a supposed anhydrous condition, $=C^{18}H^4O^6$, may be regarded as anhydrous cinnamic acid, in which 3 equivs. of hydrogen are replaced by an equal number of equivalents of oxygen:—$C^{18}H^7O^3$ anhydrous cinnamic acid $-H^3+O^3=C^{18}H^4O^6$ anhydrous æsculetine.

When æsculetine takes up 2 equivs. of water, as is the case in the formation of the lead salt in a watery solution, it acquires the composition of moritannic acid:—$C^{18}H^6O^8$ æsculetine $+2HO$ $=C^{18}H^8O^{10}$ moritannic acid, with which æsculetine has these properties in common, that it is coloured green by peroxide of iron, and forms yellow salts with oxide of lead and several other bases.

Phloridzine is resolved, by the action of acids, into sugar and

phloretine. Phloretine has the composition $C^{30}H^{14}O^{10}$. Amygdaline, which occurs in plants most closely allied to those yielding phloridzine, is decomposed into sugar, hydrocyanic acid and oil of bitter almonds. The *Spiræaceæ*, which are so closely allied to the plants producing phloridzine and amygdaline, contain salicylous acid; or, at least, this substance may be obtained from them by distillation with water. Salicylous acid is oil of almonds to which 2 equivs. of oxygen have been added:—$C^{14}H^6O^2$ oil of bitter almonds $+2O=C^{14}H^6O^4$ salicylous acid.

Phloretine is oil of almonds which has taken up carbonic acid and water, and assimilated their elements without elimination of oxygen:—$C^{30}H^{14}O^{10}$ phloretine$=2(C^{14}H^6O^2)$ oil of bitter almonds $+2CO^2+2HO$.

Æsculetine is oil of almonds which has taken up carbonic acid, with separation of the fourth part of the oxygen of the latter; or, which is the same thing, oil of almonds united with oxalic acid:—$C^{18}H^6O^8$ æsculetine $=C^{14}H^6O^2$ oil of bitter almonds $+2(C^2O^3)$ oxalic acid.

Saligenine contains the elements of oil of almonds, with the addition of 2 equivs. of water:—$C^{14}H^8O^4$ saligenine$=C^{14}H^6O^2$ oil of bitter almonds$+2HO$.

Salicine contains saligenine and a hydrate of carbon$=C^{19}H^{10}O^{10}$. Populine contains saligenine and benzoic acid (which has the same composition as salicylous acid) united with a hydrate of carbon:—$C^{40}H^{22}O^{16}$ populine$=C^{14}H^6O^4$ benzoic acid$+C^{14}H^6O^2$ saligenine$+C^{12}H^{10}O^{10}$ hydrate of carbon. According to Piria, it splits into sugar, saligenine and benzoic acid, taking up 4 equivs. water. In this respect, salicine, populine, amygdaline, phloridzine, and æsculine stand in an extremely intimate connexion.

Trommsdorff gives the formula $C^{16}H^9O^{10}$, or, which is the same thing, $C^{32}H^{18}O^{20}$, for æsculine. The per-centage composition, which corresponds with this formula, is nearly the same as that required for the formula given by the authors, $C^{42}H^{24}O^{26}$:—

		Found.		Calculated.
Carbon	42	52·07	32	51·89
Hydrogen	24	4·96	18	4·86
Oxygen	26	42·97	20	43·25

According to the authors' formula, the carbon is about 0·18 per cent., and the hydrogen about 0·1 per cent. more than according to Trommsdorff's calculations. On the average of his analyses, he found rather more carbon than is required by his formula, and his hydrogen agrees with the quantity found by the authors.

If Trommsdorff's formula be regarded as the correct expression of the composition of æsculine, its splitting into æsculetine and hydrate of carbon would take place in the following manner:—$C^{32}H^{18}O^{20}$ æsculine$=C^{12}H^{11}O^{11}$ hydrate of carbon$+C^{20}H^7O^9$ æsculetine.

In this manner æsculine would be brought into close agreement with Kawalier's arbutine. Arbutine, dried at 212° F.$=C^{32}H^{22}O^{19}$.

It is decomposed by emulsine into $C^{20}H^{10}O^7$ arctuvine, and $C^{12}H^{14}O^{14}$ grape-sugar, with assimilation of 2 equivs. of water.

Arctuvine $= C^{20}H^{10}O^7$ is distinguished from æsculetine $= C^{20}H^7O^9$ by containing 3H more and 2O less than that substance, according to this formula. Æsculetine might be regarded as a substance analogous to oil of turpentine, in which 9 equivs. of hydrogen were replaced by the same number of oxygen:—$C^{20}H^7O^9$ æsculetine $= C^{20}H^{16} - 9H + 9O$.

The formula $C^{20}H^7O^9$ however requires an amount of carbon and hydrogen which does not agree well with the analyses of æsculetine:—

		Calculated.
Carbon	20	60·30
Hydrogen	7	3·52
Oxygen	9	36·18

But 60·51, 60·73, 60·78 per cent. of carbon and 3·62, 3·51, 3·47 per cent. of hydrogen were found, consequently more carbon and less hydrogen than corresponds with the formula.

Fraxinine.—Keller discovered a crystalline substance, which he regarded as an alkaloid, in the bark of *Fraxinus excelsior*. Buchner gave the name of *fraxinine* to this substance. It is obtained by decoction of the bark with water, then precipitating the decoction with basic acetate of lead, filtering, removing the lead by sulphuretted hydrogen, filtering and evaporating the fluid: the fraxinine crystallizes in prisms of a bitter taste.

To prepare this substance for investigation, ash-bark was extracted with water, the decoction precipitated with neutral acetate of lead, the precipitate separated by filtration, the filtered fluid precipitated with basic acetate of lead and filtered, then treated with sulphuretted hydrogen, and the sulphuret of lead separated by filtration. The fluid was then evaporated until there remained a bitter brownish-yellow extract, in which acicular crystals made their appearance. As these could not be readily separated from the mother-liquor by mechanical means, the extract was treated with boiling alcohol, which dissolved the crystals, and took up but small quantities of the other constituents, by which it acquired a wine-yellow colour. The alcoholic extract furnished slightly bitter crystals on evaporation; these were dissolved in alcohol, and treated with animal charcoal. In this manner, perfectly colourless crystals of a substance which in its taste and all its properties possessed the greatest resemblance to mannite were obtained. Analysis showed that this substance was really mannite:—

Carbon	39·38	6 =	36	39·55
Hydrogen	7·64	7	7	7·69
Oxygen	52·98	6	48	52·76

The fraxinine therefore does not always occur in the bark of the ash, or else it is not generally to be obtained crystallized in the above manner. That a bitter principle is contained in the bark is certain, but whether or no it can be obtained in a crystalline form

must be ascertained by further observations. The authors will shortly give the results of their investigations of some other bitter principles.

Rochleder then gives the following summary of the substances which separate into a hydrate of carbon and one or two other products, when brought into contact with emulsine or dilute mineral acids at a high temperature:—

First Group.

Amygdaline.—The action of emulsine decomposes this substance into hydrocyanic acid, oil of bitter almonds and grape-sugar. (Wöhler and Liebig.)

Salicine.—This substance is resolved, by the action of emulsine, into saligenine and grape-sugar. (Piria.)

Phloridzine.—The action of diluted sulphuric acid and heat separates this substance into phloretine and grape-sugar. (Stass.)

Rhodeoretinic Acid.—Under the action of muriatic acid, this substance gives rhodeoretinole and grape-sugar. (Kaiser.) By the action of dilute sulphuric acid at a high temperature, and also by contact with emulsine, it is split into rhodeoretinolic acid and grape-sugar. (Mayer.)

Ruberythric Acid is resolved, by the action of mineral acids, but not by emulsine, into alizarine and grape-sugar. (Rochleder.)

Arbutine.—The action of emulsine splits this substance into arctuvine and grape-sugar. (Kawalier.)

Populine.—This substance is decomposed by the action of alkalies into benzoic acid and salicine, but does not change by synaptase. (Piria.)

Æsculine separates, by the action of dilute mineral acids at a high temperature, into æsculetine and sugar. (Rochleder and Schwarz.)

Second Group.

Caincic Acid.—The action of dilute mineral acids at a high temperature resolves this substance into kinovic acid and sugar. (Rochleder and Hlasiwetz.)

Kinovatannic Acid.—This acid is split, by the action of dilute sulphuric acid at an elevated temperature, into kinova-red and sugar. (Hlasiwetz.)

Gallotannic Acid.—The action of dilute sulphuric acid at an elevated temperature splits this acid into gallic acid and sugar. (Strecker.)

The substances brought together in the first group differ from those of the second in being either quite neutral, as amygdaline, salicine, phloridzine, arbutine, populine and æsculine, or possessing only extremely weak acid properties, as ruberythric acid. Rhodeoretinic acid alone possesses the nature of an acid more distinctly. All these bodies have this in common, that their atomic weight is either not to be determined by their combinations with bases, or if it be determinable, it is very high, and corresponds with the formulæ accepted for these bodies.

The members of the second group behave differently. Their atomic weight may be determined by the analysis of their salts.

The members of the first group contain a hydrate of carbon, which contains 12 equivs. of carbon. This becomes converted into sugar by assimilation of water. These substances may be distinguished by Laurent's name of *glucosamides*.

The substances of the second group contain no hydrate of carbon with 12 equivs. of carbon. Their atomic weight must otherwise be at least twice or three times as high as that shown by the analysis of their salts. It has never occurred to any one to multiply the formula of alcohol five-fold, and write $C^{20} H^{30} O^{10}$, because naphthaline, which contains C^{20}, is produced during the passage of the vapour of alcohol through a heated tube. The fact that these acids furnish a hydrate of carbon with 12 equivs. of carbon under certain circumstances, by no means proves that they contain such a hydrate already formed.

Potato fusel-oil, treated with sulphuric acid, gives $C^{40} H^{40}$; nevertheless it has the formula $C^{10} H^{12} O^2$, and not $C^{40} H^{48} O^8$.

Why these, and probably several other acids, furnish sugar when exposed to the action of dilute mineral acids at high temperatures, whilst many other acids do not do so, is unknown, and cannot be explained by arbitrary alterations in the formulæ. It is equally unknown why many substances furnish a product of a similar percentage composition, as sugar, hydrate of acetic acid, by dry distillation, whilst other allied bodies give no trace of that substance under similar circumstances.

If we calculate new formulæ for these supposed acids, as has been done by Strecker for the tannic acids, starting from the assumption that they contain a hydrate of carbon with 12 equivs. of carbon, the author objects that we shall in future have two irreconcileable formulæ for each of these acids, one derived from its salts, and a second from the products of its decomposition.

The author also disapproves of Laurent's mode of proceeding. Laurent has recently developed a theory upon the tannic acids, in which he starts from the supposition, that all the acids allied to gallic acid must, like it, contain 5 equivs. of oxygen, and that all those corresponding with gallotannic acid must, like this, contain 26 equivs. of oxygen (according to the formula of gallotannic acid given by Laurent).

After the author had become acquainted with several acids, which are usually called tannic acids, and perceived that they, as well as all other known acids of this kind, were constituted according to one or other of the formulæ $C^{14} H^8 O^n$, $C^{14} H^6 O^n$, or $C^{18} H^8 O^n$, which latter very readily furnishes an acid of the formula $C^{14} H^7 O^n$ or $C^{14} H^6 O^n$, he came to the conclusion, that the similarity of these acids was founded in this equal quantity of carbon and nearly equal amount of hydrogen, just as he believed the similarity of potash and soda to arise from that of potassium and sodium, and the difference between the oxides of manganese and mercury from that between those two metals.

Laurent however puts forward as the cause of the similarity their equal amount of oxygen, so that he renders it quite unintelligible how indigo, alcohol, peroxide of lead, and oil of bitter almonds should be such very dissimilar bodies, seeing that they all contain 2 equivs. of oxygen. Perhaps in future we should write alcohol $=C^6 H^9 O^3$; oil of bitter almonds, $C^{28} H^{12} O^4$; and peroxide of lead, $Pb^3 O^6$!

The author adds, that the formulæ of the tannic acids may perhaps undergo some alteration hereafter, but hopes that this may be done by investigation.—*Sitzungsb. der Akad. der Wiss. zu Wien*, Dec. 1852 and Jan. 1853.

On the Presence of Formic Acid in the Human Secretions. By DUGALD CAMPBELL*.

The production of formic acid in the gradual decay or oxidation of many organic substances is a fact well known and admitted; still its formation in the animal organism is much doubted. Prof. Lehmann, in his valuable work upon Physiological Chemistry†, says, "It has only as yet been positively proved to exist preformed in ants." Indeed Lehmann seems to think that they, the ants, assimilate it from the food which they eat; for afterwards, in discussing the origin of formic acid in these animals, he says, "It is by no means certain that they produce formic acid, for we know that juniper berries and the cones of several kinds of pine contain formic acid, and that these substances are much sought after by ants."

Considering how favourable the animal organism appears to be for the gradual decay or oxidation of organic substances, consequently the production of acids, and that a number of acids of the same family or group as formic acid have already been detected in the emanations from that organism, I am at a loss to say how formic acid should have escaped notice. My impression was, that it might only be produced in the animal organism in very small quantity; and the nature of the acid being so highly volatile, it might find its way out through the pores of the skin, and not into the animal fluids. Still, I had never known of formic acid having been observed in any exudations (although since my experiments I can scarcely now doubt of its presence in them), and I had hoped, by a careful examination of some of the fluids either of healthy or unhealthy persons, to detect it; but until recently it had escaped my notice.

The first opportunity I had of observing it was in the vomit of a male patient suffering from phthisis, with abscess in the kidneys. The vomit was of a golden straw colour, strongly acid to test-paper, with an odour resembling sour bread. The method of examination was as follows:—The vomit was filtered into a small retort, and distilled by means of a water-bath as long as the distillate was acid. On examining this acid liquid, slight traces of some of the characteristics of formic acid were observed; still, these indications might

* Communicated by the Author.

† Vol. i. p. 50. Translated for the Cavendish Society.

arise from some aldehyde compound; and in order to make sure of the removal of every trace of such compound, the liquid was neutralized with a dilute solution of carbonate of soda, the whole evaporated by a water-bath to perfect dryness, the residue dissolved in a few drops of water and evaporated to dryness, and this repeated until no traces of odour were left. The residue was now dissolved in a little water, the solution transferred into a retort, slightly acidified with dilute phosphoric acid, and distilled by a water-bath; an acid colourless liquid came over, which, when heated with salts of silver, reduced them to the metallic state; likewise, heated with corrosive sublimate, produced calomel; and when neutralized with an alkali, gave with solutions of sesquioxide of iron a blood-red solution,—the well-known actions of formic acid and formiates upon these substances.

In the above experiment, dilute phosphoric acid was employed to neutralize the soda salts, as sulphuric acid might be objected to, from its action upon some organic compounds when heat is applied producing formic acid.

My second experiment was upon the vomit of a female similarly afflicted, namely phthisis, with abscess in the kidneys. The vomit was characteristic of the last in colour, acidity and odour. I adopted the same method of analysis as in the foregoing case, and I obtained similar results.

My next experiment was upon the vomit from a boy, ten years of age, ill with hooping-cough, and said to have some chronic disease of the kidneys. It was of a darker colour than the two previous, but not so acid to test-paper; the odour was suggestive of raisins. The examination was conducted in a similar manner to the two previous ones, with the exception of dilute hydrochloric acid being used to neutralize the soda salts before distillation, instead of dilute phosphoric acid. The results of the examination gave distinct evidence of formic acid.

Of the three cases just described, the last contained much the smallest amount of formic acid; but still the acid was in such quantity, that with moderate care it could not fail to be detected.

I submitted a few more vomits, supposed to be from healthy persons, to examination, following the method of analysis described above, and in every one I detected formic acid, although the quantity in each differed considerably. A very small quantity was found in the vomit from a woman shortly after labour, and still less in that from a baby at the breast, about two months old.

No medicines in either case had been given to cause vomiting, and the vomits were all perfectly fresh when experimented upon.

The examinations have been limited from the difficulty I experienced in procuring vomits; still, judging from my experiments, I should say, few vomits will be found that do not contain formic acid, although the quantity appears very variable—in some a considerable quantity, in others a trace.

From having found formic acid so general in the vomits of healthy as well as unhealthy persons, it next occurred to me to look for it in

the urine; but how to proceed was a more difficult task, for I did not by any means like to render the urine acid by a mineral acid before distillation, in case I might in some way assist in the formation of formic acid, by the action of a mineral acid and heat upon some of the constituents of the urine. In the course of my experiments, I observed, in distilling dilute solutions of formiate of ammonia containing carbonate of ammonia by water-bath heat, that, besides carbonate of ammonia in the distillate, I obtained some formiate of ammonia; and it occurred to me that the ordinary distillate from urine containing carbonate of ammonia might likewise be found to contain formiate of ammonia.

My experiments were all made upon fresh urine, acid to test-paper, and from persons in the ordinary habit of life and supposed to be healthy.

The urine was distilled by water-bath heat; the distillate, which was little more than one-fourth the original quantity of urine taken for the experiment, was acidified by phosphoric acid very dilute, and distilled by same heat; a slightly acid liquid came off, which was neutralized with a dilute solution of carbonate of soda, and evaporated to dryness by a water-bath, the residue dissolved in a small quantity of water and evaporated to dryness, and this repeated until no odour was perceptible in the residue, which was then dissolved in a few drops of water, washed into a retort, and slightly acidified with dilute phosphoric acid: on distilling by a water-bath, an acid distillate was obtained, which, when heated with solutions of salts of silver and mercury, gave the characteristic actions of formic acid upon these substances; and when neutralized with an alkali, gave with solutions of sesquioxide of iron a blood-red colour.

This experiment was repeated several times upon different quantities of urine, and formic acid was found in all the results. Sometimes hydrochloric acid was substituted for the phosphoric acid, but it made no difference.

By following the above process, it is difficult to say whether all the formic acid in the urine comes over in the ammoniacal distillate; if so, the quantity in the urine I experimented upon was very small. I used several gallons in each experiment, but my object was not so much to ascertain the quantity as really to ascertain the presence of formic acid.

On the Cause of the Luminosity of certain Bodies when heated. *By* A. Schrötter.

Naturalists are still at variance with regard to the luminosity of bodies at ordinary temperatures. Schrötter originally intended only to institute researches into the luminosity of phosphorus, but was afterwards led to examine whether similar phænomena are not presented by other bodies; this has been shown to be the case with sulphur, selenium and arsenic.

Berzelius considered that phosphorus only gave light in consequence of evaporation. Fischer, on the other hand, ascribed its

luminosity to a gradual oxidation. Marchand concluded from his investigations that phosphorus emits light from both causes—evaporation and oxidation.

Schrötter denies the correctness of several of the experiments instituted by Marchand, and shows in the following investigations that phosphorus is luminous only in consequence of oxidation.

Under the bell of the air-pump the luminosity of phosphorus is at first somewhat increased, but on further exhaustion it continues unchanged. When the barometer has sunk to 1 millim., there rises from the phosphorus, about 10–15 minutes after the commencement of the exhaustion, a luminous flame: this soon fills the whole of the bell-glass with a luminous, opake, bluish atmosphere, through which the phosphorus cannot be recognised. In from half a minute to a minute afterwards this luminous atmosphere contracts again about the stick of phosphorus, which then reappears; everything now remains dark, even when the bell-glass is warmed. If the exhaustion be continued after the phosphorus has begun to be luminous, nothing is produced but a light alternately in each glass cylinder at each stroke of the piston. The introduction of a very small quantity of air into the bell causes this to become filled for a short time with a luminous atmosphere: this is a beautiful experiment, which may be repeated three or four times.

If exhaustion alone were the cause of the luminosity, it must appear in the bell-glass instantaneously on each up-stroke of the piston, for it is visible in the cylinder, which can only take place when phosphoric gas, given off by the phosphorus under the bell-glass, passes into the cylinder. The phænomenon may be explained without difficulty by oxidation. Thus, as phosphorus requires very little oxygen to become luminous, and as no phosphoric gas can be produced in the presence of free oxygen without becoming oxidized immediately, the phosphorus continues to shine for some time even with considerable exhaustion of air. At last, however, the quantity of oxygen must be so reduced, that it is overbalanced by the phosphoric gas formed; the latter will then become diffused in the bell-glass, taking up however at the same time the last portions of oxygen with production of light: in this manner the phænomena above described will be produced.

In a Torricellian vacuum of 265 cub. centims., phosphorus did not exhibit the least luminosity (in contradiction to the statements of Berzelius) even when the tube was held as obliquely as possible, by which the vacuum was diminished about half, the phosphorus heated to boiling, and the tube then rapidly brought back into a vertical position. The phosphorus was sublimed into the upper part of the tube, where it attached itself in thin shining laminæ. Phosphorus can therefore evaporate very quickly without becoming luminous; and this negative result is conclusive, because a luminosity continuing during some time could be explained by the supposition that some air was present, and would not consequently have spoken decisively in favour of the evaporation view.

When phosphorus was introduced into a bell-glass, moistened internally and closed with mercury, containing about 800 cub. centims. of pure hydrogen gas produced by electrolysis, it gave out light for about a quarter of an hour. The bell-glass was then surrounded with hot water, so as to raise the temperature to 176°–194° F., when not the least luminosity was produced, although such a rapid evaporation of the phosphorus took place, that the walls of the glass were covered with fine globules of sublimed phosphorus. This negative experiment also is conclusive against the evaporation view. The luminosity at the commencement arises evidently from the presence of a small quantity of air, the complete removal of which from so large a bell-glass is quite impossible.

As Marchand affirmed that the luminosity of phosphorus continued without interruption even in gases which contained no trace of oxygen when these were only passed over it, the author made this experiment with hydrogen gas obtained both by electrolysis and by the ordinary method with zinc and sulphuric acid. The gas produced by electrolysis passed from a Bunsen's flask through a horizontal tube cemented to it; and the arrangement was so contrived, that the whole apparatus, before the commencement of the evolution of hydrogen gas, was filled with fluid, so that the gas had to pass through no air. No india-rubber tube was employed for the union, but the whole apparatus consisted as it were of one piece. The phosphorus was not in the least luminous, even when it was considerably heated.

In the experiments with hydrogen prepared in this manner, the arrangement was so contrived that the gas was first of all rendered completely pure and inodorous by caustic potash, sulphuric acid, &c., and then passed into a tube about 2 metres in length, the first half of which, or that nearest the apparatus for the evolution of the gas, contained copper-turnings which had been previously carefully cleaned and heated in hydrogen gas; whilst the second half, which was closed by means of a bent tube, the end of which dipped into water, contained the phosphorus. This portion of the tube projected through a hole into a dark room, whilst the remainder of the apparatus remained outside. The phosphorus continued luminous even after the gas had been passing uninterruptedly through the tube for more than six hours, and would apparently have continued so, as long as any of it remained; but when the copper-turnings were heated to a slight red heat, the luminosity of the phosphorus immediately disappeared, re-appearing as brightly as before on the copper being allowed to cool.

As long as the copper was heated, so as to take up oxygen, and the phosphorus was not luminous, the cork through which the tube dipping into the water passed was luminous on its inner surface; when the stream of gas was strong, the bubbles were also luminous; but as the copper cooled and the phosphorus became luminous, the luminosity of the cork was no longer visible. Thus when the phosphorus is not luminous, the gas in passing takes up phosphoric gas,

which, meeting with a thin layer of oxygen on the inner surface of the cork (penetrating by diffusion), gives rise to the luminosity of that part of the apparatus. But as soon as the phosphorus becomes luminous, it consumes the small quantity of oxygen contained in the gas, and no more phosphoric gas reaches the cork.—*Sitzungsber. der Akad. der Wiss. zu Wien, Math. Naturw.*, p. 414.

Upon Cynuric Acid. By J. Liebig.

In the researches instituted by Prof. Bischoff into the amount of urea contained in the urine of the dog, this fluid was frequently examined for uric acid, without the discovery of even traces of it.

In these experiments a precipitate was deposited, and that but sparingly, from the urine of many days, which was difficult to filter on account of its fineness; and it appears that this deposit consists for the most part of a hitherto-unknown acid, for which I propose the name of *cynuric acid* in allusion to its origin.

When the impure coloured deposit from the urine is dissolved in lime-water, diluted with water, heated, and then mixed with muriatic acid, the cynuric acid separates in very fine colourless needles, which have a silky lustre and redden litmus-paper. The acid separates from concentrated solutions in a pulverulent form. When heated in a glass tube, it melts, forming a brown fluid, which, if the heat be continued, becomes completely sublimed, leaving only a trace of cinder. The sublimate is white, silky, crystalline; it is readily soluble in alcohol, which serves to distinguish it from the original acid.

Cynuric acid is readily distinguished from uric acid by its solubility in muriatic acid; the precipitate which is produced by the addition of muriatic acid to the alkaline solutions of the acid disappears on the addition of an excess of muriatic acid. Cynuric acid dissolves readily in boiling muriatic acid, diluted sulphuric acid and nitric acid, in the latter without visible signs of change; the hot saturated solutions set on cooling into a jelly of short, very shining needles. It is dissolved by concentrated sulphuric acid in the cold without change; on the application of heat, a slight brownish discoloration is produced; the addition of water then produces a beautiful citron-yellow, amorphous precipitate, which is sometimes mixed with crystals of unchanged acid. Cynuric acid is readily dissolved by the caustic alkalies, and with the aid of heat by their carbonates and by lime and baryta water; a sufficient quantity of it destroys all alkaline reaction. By the evaporation of these solutions, well-crystallized salts are obtained; the lime salt forms short hard needles, grouped in a stellate form; the baryta salt, pearly laminæ with a plumose arrangement; both salts are difficult of solution in water. A solution of the acid in ammonia furnishes with nitrate of silver a thick white precipitate, which is not soluble by heat.

Cynuric acid is insoluble in alcohol and æther.

I was unwilling to sacrifice the small quantity of the acid at my

command for the purpose of analysis, because it appeared to me that an acquaintance with the composition of a substance which appears to occur but rarely and only in small quantities in the urine was of less consequence than the knowledge of the fact of its occurrence and of the properties by which it may be recognised. From the experiments which I instituted to ascertain the quantity of nitrogen, it appears that the acid contains no nitrogen, or so little that the small quantities with which I was able to operate were not sufficient to furnish a distinct reaction.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 125.

Upon Oxylizaric Acid (*Purpurine*). *By* H. Debus.

In a memoir communicated to the Royal Society of London, Schunck has described some investigations, which lead him to the supposition that the red colouring matter of the madder root, described by me as oxylizaric acid, and by other chemists as purpurine, is a mixture of alizarine and a resinous body. Oxylizaric acid is distinguished from alizarine not only in colour and composition, but also by a much greater solubility in hot solution of alum.

Schunck states that a mixture of alizarine and β-resin dissolves much more readily in solution of alum than either of the ingredients by itself, and that the violet colour of the solution of alizarine is changed by the β-resin to the characteristic red of solutions of oxylizarine. He consequently believes that oxylizaric acid is an impure alizarine.

The oxylizaric acid investigated by me was very beautifully crystallized, and samples prepared from various sorts of madder gave on analysis concordant numbers; they exhibited generally all the peculiarities which one might expect from a pure substance. The addition of resin to alizarine renders its crystallization difficult, whilst oxylizaric acid is readily obtained in regular forms. Although the above-mentioned supposition appeared thus to have but little [illegible] through it, yet I thought it worth while to institute some researches [illegible] ratus [illegible] this point. According to Schunck, when the mixture of ali- [illegible] after [illegible] and β-resin is dissolved in alcohol, and acetate of copper [illegible] mo[illegible] to the solution, the resin is thrown down in combination with [illegible] lo[illegible] oxide of copper, whilst the alizarine remains in solution. Con- [illegible] l[illegible]quently if crystallized oxylizaric acid consists of resin and aliza- [illegible]ne, it must be capable of decomposition into these constituents by [illegible]eans of acetate of copper.

A quantity of oxylizaric acid was accordingly dissolved in alcohol, and an excess of an alcoholic solution of acetate of copper added to the clear fluid. The liquid filtered from the resulting dark brown precipitate contained neither alizarine nor any other colouring matter. The precipitate, on the other hand, which ought to consist of β-resin and oxide of copper, gave, after careful washing, decomposition with muriatic acid and solution of the separated colouring matter in alcohol, instead of resin, unchanged oxylizaric acid. In

this manner I obtained the colouring matter very pure, in beautiful reddish-yellow needles, which dissolved readily in solution of alum, and fused when heated by themselves into a reddish-yellow fluid, which on cooling solidified into a mass of long needles united concentrically, of the colour of ferrocyanide of potassium.

0·427 grm. of the crystallized colouring matter lost 0·021 grm. of water at 212° F., or 4·9 per cent. The formula $C^{18} H^6 O^6 + HO$ requires 5·2 per cent. of water. Crystallized alizarine, on the other hand, contains 18 per cent. of water, which goes off at 212° F. There can consequently be no doubt of the existence of oxylizaric acid.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 117.

ANALYTICAL CHEMISTRY.

On the Determination of the Ammonia contained in Waters. *By* M. Boussingault.

Boussingault refers to the necessity of determining the quantities of ammonia contained in well-water, river-water, &c. Since the time (1802) when De Saussure ascertained the first traces of ammonia in the air, since Brandes (1825) discovered it in rain-water, and especially since the time when Liebig distinctly proved this occurrence of ammonia, no complete investigations into the quantity of ammonia contained in natural waters has yet been made.

Boussingault has now begun to determine the ammonia in such waters by means of a distillatory apparatus. He regards it as certain that a water charged with a small quantity of ammonia will have given off the whole of this with the watery vapour when two-fifths of the water have distilled over.

We may, consequently, by submitting large quantities of water, as 10 litres or more, to a preliminary distillation, obtain a concentrated fluid, so as to treat this in the still set apart for the determination of the ammonia. Where the water is not too poor in ammonia, it may be placed in the apparatus itself.

The apparatus consists of a retort capable of containing 2–3 litres. A litre of the water to be examined is put into this, if necessary previously concentrated. The cooling of the distillate is effected by means of a glass worm-tube. One-fifth is distilled off, and the quantity of ammonia contained in it ascertained, according to Peligot's method of determination of nitrogen by means of a solution of sulphuric acid of known strength. A second fifth is then distilled. In this there is generally no more ammonia, and the quantity found in the first portion is usually correct.

The normal solution of sulphuric acid for the determination of the ammonia is so composed that 5 cub. centims. of this fluid shall be saturated by 0·0106 of ammonia. As the alkaline fluid which serves for the testing of the solution is so far diluted that 33 cub

centims. of it saturate the 5 cub. centims. of dilute acid, 1 cub. centim. of the alkaline fluid represents 0·00032 of ammonia; and as the burette is divided into tenths of a cubic centimetre, one division represents 0·000032 of ammonia.

As regards the accuracy of the determination, it is necessary in this process to take care that the normal acid is first added to the fluid to be tested for ammonia, and that the alkaline fluid intended for the saturation of the acid is then poured in. Any inaccuracy must therefore arise from an error of two divisions of the burette. The determination of the ammonia can therefore only be brought within 0·06 milligrm.; but as the operation can always be performed twice, even if the errors of the two experiments do not compensate one another, the error of the method cannot exceed a tenth of a milligramme.

The author then instituted experiments to test this method. From these it appeared that distilled water to which a known quantity of ammonia had been added furnished more ammonia than had been mixed with it; so that apparently all distilled water contains ammonia. The water employed in the following experiments was distilled first with sulphate of alumina, and afterwards over potash, to remove any ammonia and carbonic acid that might be contained in it. In the following table, the first column gives the number of the experiment, the second the quantity of ammonia added to the water, the third the quantity obtained from the distillate, and the fourth the difference between the two preceding:—

I.	II.	III.	IV.
1.	0·01233	0·01224	−0·00009
2.	0·00036	0·00037	+0·00001
3.	0·01056	0·01040	−0·00016
4.	0·01130	0·01131	+0·00001
5.	0·00836	0·00840	+0·00004
6.	0·04944	0·04950	+0·00006
7.	0·00413	0·00410	−0·00003

The following is a table of the quantities of ammonia ascertained by the author in various waters:—

Month.		Ammonia in 1 litre of water. grm.	1 cub.m. of water. grm.
April.	Water from the Seine (*au pont d'Austerlitz*)	0·00012	0·12
April.	Water from the Seine (*au pont de la Concorde*)	0·00016	0·16
April.	Water from Ourcq (*fontaine du Conservatoire*)	0·00073	0·73
May.	Water from Ourcq (*fontaine du Conservatoire*)	0·00003	0·03
Mar.	Water from the Canal de Loing (*à Montargis*)	0·00032	0·32
April.	Water of the Bieber (*au Pont-aux-Tripes*)	0·00261	2·61
April.	Water of the Arcueil	0·00017	0·17
April.	Water from a well near Andilly (*Montmorency*)	0·00003	0·03
May.	Water from the Lac d'Enghien	0·00007	0·07
April.	Water of a well near Guermantes (*Lagny*)	0·00000	0·00

With the exception of the Bieber, which is rather an outlet for the numerous industrial establishments than a river, all the above waters contain less ammonia than rain-water; the well near Lagny (*Seine-et-Marne*) contained none at all, or none that could be ascertained.

In the rain-water collected on the terrace of the Observatory at Paris, Barral found on an average 3·35 milligrms. of ammonia to 1 litre of water. The greatest quantity that he met with was 5·45 milligrms. Boussingault has hitherto made but few determinations of the ammonia in rain-water, but these agree well with Barral's. Thus in the first week of April he found 4·34 milligrms. in 1 litre of rain-water at Paris. This is twenty-seven times as much as existed at the same time in the Seine water. On the 7th of May the rain-water contained 0·0032 grm. in 1 litre.

The water of the Lac d'Enghien, according to the above table, contains a tenth of a milligramme of ammonia in 1 litre. A spring which rises near this lake contains 5·06 milligrms. Considered as bicarbonate of ammonia, this gives 0·0181 of the salt; it is possible that this assists the medicinal action of the sulphurous water of Enghien.

In 1 litre of sea-water from near Dieppe the author found 0·00020 grm. of ammonia. If we consider that two-thirds of the surface of the globe are covered with water, the sea always contains a considerable quantity of ammonia, which may return again into the atmosphere.

In places where great numbers of people live, the quantity of ammonia in the soil must increase. The investigation of the following spring-waters proves this:—

	In 1 litre. grm.	In 1 cub. metre. grm.
Spring in a garden (*Jardin de Clignancourt*) outside Paris	0·00032	0·32
Spring of a house in the *Rue du Parc-Royal*	0·00132	1·32
Spring of a house in the *Place de l'Hôtel-de-Ville*	0·03435	34·35
Spring of a house *Quai de la Mégisserie*, No. 30	0·03033	30·33
Spring of a house *Quai de la Mégisserie*, No. 28	0·03386	33·86
Spring of a house in the *Rue de la Tabletterie*	0·00026	0·26

The Parisian well-water is not drinkable. It is very hard, decomposes soap, and is not fit for boiling vegetables. It has in general no smell; the great quantity of ammonia contained in this water may nevertheless arise from dung or other decaying organic matters.

The author collected some snow in March, immediately after its falling on a terrace, and thirty-six hours afterwards some from the fertile earth of a garden. On determining the ammonia contained in the water resulting from the melting of the snow, he found in the

	In 1 litre.	In 1 cub. metre.
Snow from the terrace	0·00178	1·78
Snow from the garden	0·01034	10·34

The large quantity of ammonia in the snow from the garden must apparently have passed into it from the soil.—*Comptes Rendus*, vol. xxxvi. p. 814.

On the Employment of Picric Acid for distinguishing Vegetable and Animal Fibres in Stuffs. *By* Dr. J. J. Pohl.

The author employs a solution of picric acid in water or alcohol for the distinction of vegetable from animal fibre. The original watery solution is diluted with 6 parts, the alcoholic with 15–20 parts of water; a small piece of the stuff to be examined is then dipped in the solution. In from six to ten minutes at ordinary temperatures, or in two or three minutes when the fluid is heated to 104° F., the stuff or yarn is taken out and washed with water. Stuffs made entirely of cotton or linen appear perfectly white after washing; but those consisting of wool, or silk, or other animal fibres, acquire a yellow colour, it being understood that undyed stuffs are to be used in the experiment. In mixed stuffs the animal fibres appear coloured, whilst the vegetable fibres remain white. The test is so exact, that even in those stuffs or yarns in which the individual threads consist of both substances, the proportion of animal and vegetable fibre can be exactly ascertained by means of a lens. By the employment of an ordinary thread-counter, the number of vegetable and animal fibres in these mixed fabrics may be ascertained with sufficient exactness.

This test may also be employed with most dyed stuffs; at least it may be applied to orange, red, fawn colour, rusty yellow, violet, every kind of blue, and some browns. Thus, as the mordants usually employed, as alumina and salts of tin, and lead and iron compounds, do not produce any essential change in the yellow colour of picric acid, but only deepen it more or less, stuffs dyed with the above-named colours undergo no remarkable change by being dipped in the test-solution if they consist of vegetable fibre; but a change always takes place when animal fibre is present, and this will always indicate with perfect certainty whether a stuff consists of animal or vegetable fibre or of a mixture of both. Thus wool dyed red becomes changed by picric acid into orange-red or orange according to the shade of the original colour, whilst rusty yellow becomes bright yellow, blue colours green, and green greenish-yellow.—*Sitzungsb. der Akad. der Wiss. zu Wien*, ix. p. 387.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Alkaloids of the Cinchonas. *By* L. PASTEUR.

IT is about half a century since *cinchonine*, previously noticed by Dr. Duncan of Edinburgh, was first isolated by Gomès, a physician of Lisbon. To its presence he attributed the action of the cinchona barks; but he misunderstood its alkaline nature, which was not thoroughly appreciated until about 1820 by MM. Pelletier and Caventou; at this period these chemists also discovered *quinine*. About twelve years afterwards, two other French chemists recognised a third alkaloid, to which they gave the name of *quinidine*, in the yellow jesuit's bark. In the year 1829, Sertuerner, who had already become celebrated by his discovery of morphine, pointed out the existence, in the mother-waters of sulphate of quinine, of an uncrystallizable base, which he called *quinoidine*, and to which he attributed wonderful febrifuge properties.

The general properties of quinine and cinchonine are pretty well known; but with regard to quinidine and quinoidine, the most contradictory opinions prevail. I believe I have got rid of all the difficulties. The results of my labours also exhibit quite new molecular relations between the various alkaloids of these barks. The following are the new facts at which I have arrived.

1. *Cinchonicine.*—When cinchonine in any saline combination is exposed to the action of heat, it is converted into a new base isomeric with, but quite distinct from cinchonine. I call it *cinchonicine*. All the salts of cinchonine may serve for the preparation of cinchonicine; but in order that the conversion may be easily and completely effected, it is necessary to place the salt in certain conditions. In general, when salts of cinchonine are heated, they fuse and become decomposed immediately; and if the fusion of the salt be not effected by some means at a temperature sufficiently distant from the point of decomposition, the cinchonicine will certainly be formed, but destroyed immediately by the further action of the heat. Ordinary sulphate of cinchonine, for instance, when heated directly, becomes fused and then immediately destroyed, furnishing a fine red resinous matter, which is a product of the alteration of cinchonicine. But if a little water and sulphuric acid be added to the sulphate before subjecting it to the action of heat, it remains fused even after the expulsion of all the water at a low temperature; and

it is sufficient to keep it in this state at a temperature of 248°–266° F. for three or four hours, to convert it entirely into sulphate of cinchonicine. The production of colouring matter is very trifling,—nearly inappreciable.

I prove, by facts which will be accepted by all chemists, that if heat plays a great part in this transformation of cinchonine, the vitreous, resinoid state of the product has a certain influence; and the present case of isomerism certainly related to those metamorphoses, of which mineral chemistry offers us several examples, such as soft sulphur, red phosphorus, and vitreous arsenious acid.

2. *Quinicine.*—All that has been stated in the preceding section with regard to cinchonine applies equally to quinine. Any salt of this base, heated in the same manner as the salt of cinchonine, is also converted into a new base isomeric with quinine. I call this new base *quinicine.* The most convenient mode of preparing it consists in adding a little water and sulphuric acid to the sulphate of quinine of commerce, and exposing it to the heat of an oil-bath of 248°–266° F. for three or four hours; the salt remains fused even after the expulsion of all the water, and becomes completely converted into sulphate of quinicine, with a very minute production of colouring matter.

As regards the general properties of cinchonicine and quinicine, they offer well-marked analogies with the isomeric bases from which they are derived. They especially present the greatest resemblance to one another. Both of them are nearly insoluble in water, but very soluble both in absolute and ordinary alcohol. They both combine readily with carbonic acid, and expel ammonia from its saline combinations in the cold. They are both precipitated from their solutions in the form of fluid resins in the same manner as quinine under certain circumstances. They both deviate the plane of polarization to the right. They are very bitter and febrifuge.

3. *Quinidine.*—The contradictions to be met with in the works of chemists with regard to this substance all arise from a fact which has escaped them, namely, that under the name of quinidine two very distinct alkaloids have been confounded; these are nearly constantly associated by mixture in commercial quinidine, if it has not been purified by several successive crystallizations. Thus the quinidine discovered in 1833 by Henry and Delondre is quite a different thing from that which is now called by that name in Germany and France, and the German product is very often mixed in considerable proportion with that discovered by Henry and Delondre. All the details of the properties and composition of these two quinidines will be found in my memoir. I will only add, that one of them, for which I retain the name of *quinidine,* is hydrated, efflorescent, *isomeric with quinine,* deviates the plane of polarization to the right, and possesses, like quinine, the character of acquiring a green colour by the successive addition of chlorine and ammonia; whilst the other, to which I give the name of *cinchonidine,* is anhydrous, *isomeric with cinchonine,* exercises a rotatory power to the left, and does not exhibit the green coloration. This is now the most abun-

dant of the two in commercial samples. It is always very easy, by exposing a recent crystallization of cinchonidine to warm air, to ascertain whether it contains any quinidine. All the crystals of the latter base effloresce immediately, retaining their shape, and standing out of a dead white amongst the clear crystals of cinchonidine. We may also recur to the character of the green coloration by chlorine and ammonia.

There are consequently four principal alkalies in the cinchona barks,—quinine, quinidine, cinchonine and cinchonidine.

4. *Action of Heat on Quinidine and Cinchonidine.*—I have submitted the two new bases quinidine and cinchonidine to the moderate action of heat, as I had done with quinine and cinchonine, and with exactly the same results; that is to say, the two new bases are converted into isomeric bases, weight for weight, with the same facility and under the same conditions as quinine and cinchonine. But, moreover, and this is undoubtedly one of the most important facts in this investigation, the two new bases obtained by the transformation of quinidine and cinchonidine are identical, the first with quinicine and the second with cinchonicine. In this manner we arrive at this remarkable result, that of the four principal bases contained in the cinchona barks, namely, quinine, quinidine, cinchonine and cinchonidine, the first two can be converted, weight for weight, into a new base, quinicine, which proves that they are themselves isomeric; whilst the two others are converted under the same conditions into a second base, cinchonicine, which proves that they are also isomeric.

The molecular relations, to which these results call the attention of chemists, take a new character when we compare the rotatory powers of the six preceding alkalies. Quinine deviates to the right, quinidine to the left—both to a considerable extent. Quinicine deviates to the right, but to a very small extent compared with the rotatory powers of the two others. The same relations are presented by the three other isomeric bodies, cinchonine, cinchonidine, and cinchonicine. Cinchonine deviates to the right, cinchonidine to the left, both considerably; cinchonicine, on the contrary, produces very slight deviation to the right. The most logical interpretation of these results is the following:—The molecule of quinine is double, formed of two active bodies, one which deviates considerably to the left, and the other very slightly to the right. The latter, which is permanent under the influence of heat, resists isomeric transformation, and remaining without alteration in the quinicine, gives this its feeble deviation to the right. The other group, which on the contrary is very active, becomes inactive when the quinine is heated so as to become converted into quinicine; so that quinicine is nothing but quinine in which one of the active constituent groups has become inactive. Quinicine would also be quinidine in which one of the active constituent groups had become inactive; but in quinidine this very active group would be right instead of left as in quinine, but still united with the same slightly active right group, which being permanent remains in the quinicine, and gives it its

weak right deviation. I might repeat all that I have said word for word, applying it to cinchonine, cinchonidine and cinchonicine, which are respectively constituted like their three congeners; they offer exactly the same relations.

5. *Quinoidine.*—I shall not enter into the detail of the experiments which I have undertaken upon quinoidine; but there is one point to which I wish to call the attention of manufacturers of sulphate of quinine and of the companies who collect the barks of cinchonas in America. Quinoidine is always a product of the alteration of the alkalies of the cinchonas. It has two distinct origins. It is produced in the operations for the manufacture of sulphate of quinine, and especially in the forests of the New World, when the wood-cutter, after stripping the bark from the tree, exposes it to the sun to dry it. Then the salts of quinine, cinchonine, &c. contained in the bark, become converted into resinous and colouring matters, which form the greater part of the quinoidine of commerce. I have ascertained, in fact, that when a salt of quinine or cinchonine in a dilute or concentrated solution is exposed to the sun even for a few hours, it becomes changed to such an extent that the liquid acquires an extremely dark reddish-brown colour. This change, moreover, is of the same nature as that which is effected by the influence of an elevated temperature. I believe, therefore, that considerable loss of quinine, cinchonine, &c. would be avoided, and that the extraction of these bases would be rendered more easy, if the bark was shaded from the light when collected, and dried in the shade. The manufacturer of quinine ought also to avoid the action of a bright light.—*Comptes Rendus*, July 25, 1853, p. 110.

On Sebacic Acid. By Henri Carlet.

Since the discovery of sebacic acid by Thenard, this acid has always been prepared by the process indicated by that illustrious chemist, that is to say, by the distillation of fat. This process only gives small quantities of sebacic acid; consequently the properties of this acid and of its compounds have been but little studied. In his researches upon castor-oil, M. Bouis has indicated a ready mode of preparing sebacic acid; at the close of his investigations he had obtained a considerable quantity of it, which he was so good as to place at my disposal. I undertook this investigation with the view of ascertaining the identity of the acid obtained by the old and new processes, and adding some new facts to its history.

The following are the principal results at which I have arrived:—

The acid obtained by both processes is the same substance; its composition, long since indicated by Dumas and Peligot, is represented by the formula $C^{20}H^{18}O^{8}$. The average of five analyses of sebacic acid gave me C=59·25, H=9·07 per cent.

Sebacic acid in a state of purity is white, solid, and fusible at 261° F. The density of the fused acid is 1·1317. It is sparingly soluble in cold, but very soluble in hot water; it is also very soluble in alcohol, æther and fatty bodies. Chlorine acts upon it only under

the influence of the solar rays; it gives rise to two products of substitution, which are represented by the formulæ $C^{20}\left(\begin{matrix}H^{17}\\Cl\end{matrix}\right)O^8$ and $C^{20}\left(\begin{matrix}H^{16}\\Cl^2\end{matrix}\right)O^8$. These two products are of a yellow colour, and of a pasty consistence at ordinary temperatures.

Treated with nitric acid, sebacic acid furnishes succinic acid.

A certain number of salts formed by sebacic acid have been submitted to analysis; their composition confirms that which has been given for the acid. The formation of acid sebates has been proved; these, with the exception of sebate of ammonia, are very readily decomposable.

A new æther has been prepared, the sebacic æther of wood-spirit, or methylosebacic æther, $C^{20}H^{16}O^6, 2(C^2H^3O)$. This substance is readily obtained by the following process:—A certain quantity of sebacic acid is dissolved in concentrated sulphuric acid, which is readily effected without any elevation of temperature; wood-spirit is then poured by little and little into the solution, shaking the mixture, and keeping it in cold water to avoid elevation of temperature; a large quantity of water is then added to separate the æther produced, which is washed first with slightly alkaline water, and afterwards with pure water; lastly, it is purified by crystallization in alcohol. Methylosebacic æther is solid at ordinary temperatures; it fuses at 78° F., and crystallizes in beautiful needles during solidification. It is heavier than water when solid, but lighter when fused; its density consequently differs very little from that of water. It has a very faint odour; at 545° F. it boils without alteration. It is decomposed by potash, giving sebate of potash and wood-spirit.

The sebacic æther of ordinary alcohol, $C^{20}H^{16}O^6, 2(C^4H^5O)$, has also been analysed. This substance is fluid at a temperature above 16° F.; it is lighter than water, and boils at a temperature of 496° F.

Lastly, I have repeated Rowney's experiments upon sebamide and sebamic acid, preparing sebamide by the action of ammonia upon methylosebacic æther, as shown by the following formulæ:—

$$\underbrace{C^{20}H^{16}O^6, 2(C^3H^3O)}_{\text{Methylosebacic æther.}} + 2NH^3 = \underbrace{2C^2H^4O^2}_{\text{Wood-spirit.}} + \underbrace{C^{20}H^{20}N^2O^4}_{\text{Sebamide.}}.$$

I have also proved the conversion of sebamide into sebamate of ammonia under the influence of water, as shown by the following formulæ:—

$$\underbrace{C^{20}H^{20}N^2O^4}_{\text{Sebamide.}} + 2HO = C^{20}H^{22}N^2O^6 = \underbrace{C^{20}H^{19}NO^6, NH^3}_{\text{Sebamate of ammonia.}}.$$

My results in other respects are completely in accordance with those of the English chemist.—*Comptes Rendus*, July 25, 1853, p. 128.

On the Action of Ammonia on the Sulphoamylate of Lime. *By* M. Berthelot.

If the sulphoamylate of lime be heated to 482° F. with an alcoholic solution of ammonia, a decomposition is produced, with formation of a salt of amylammine.

This follows from the following facts:—The substances, after having undergone the action of heat in a closed vessel for two hours, were distilled with some potash, and the fumes condensed in a watery solution of muriatic acid. This solution was evaporated to dryness, treated with absolute alcohol in the cold, evaporated again, again taken up by alcohol, and lastly mixed whilst hot with bichloride of platinum. The liquid, when cooled, deposited crystals, which furnished the following numbers on analysis:—

Carbon	19·4
Hydrogen	5·2
Platinum	33·9

The formula $C^{10} H^{13} N, HCl, PtCl^2$ requires—

Carbon	20·5
Hydrogen	4·8
Platinum	33·6

This decomposition is represented by the following formula:—

$$\left.\begin{matrix} C^{10} H^{11} O, SO^3 \\ CaO, SO^3 \end{matrix}\right\} + NH^3 = C^{10} H^{13} N, HO, SO^3 + CaO, SO^3.$$

It is entirely conformable to the assimilation established by M. Wurtz between the æthylic alkalies and the æthers. In the present case this analogy is so much the more complete, because amylammine, formed hitherto only by means of particular æthers (cyanic, hydrobromic, and their analogues), is produced during the decomposition of the sulphoamylates, exactly in the same manner as the æthers during the decomposition of the sulphovinates, sulphoamylates, &c., according to the general process indicated by M. Pelouze:—

$$\left.\begin{matrix} C^{10} H^{11} . O, SO^3 \\ CaO, SO^3 \end{matrix}\right\} + Cy . K = C^{10} H^{11} . Cy + KO, SO^3 + CaO, SO^3.$$

$$\left.\begin{matrix} C^{10} H^{11} . O, SO^3 \\ CaO, SO^3 \end{matrix}\right\} + NH^2 . H = C^{10} H^{11} . H^2 N, HO, SO^3 + CaO, SO^3.$$

The sulphovinate of baryta, heated to 482° F. with ammonia, and then treated as above, furnished a deliquescent muriate, soluble in absolute alcohol, and the platinum salt of which, treated with potash, produced an alkaline inflammable gas. It is doubtless æthylamine.—*Comptes Rendus*, June 20, 1853, p. 1098.

On some Combinations of Copper with Cyanogen. *By* A. Dufau.

The precipitate obtained by pouring a solution either of an alkaline cyanide or of hydrocyanic acid into a solution of a salt of

copper was long regarded as cyanide of copper. M. Balard was the first to announce, in 1845*, that in this reaction there was an elimination of a variable quantity of cyanogen; and that, in consequence of some circumstances not ascertained, the white protocyanide was sometimes obtained, and sometimes the yellow cyanide, the composition of which is intermediate between that of the protocyanide and that of the cyanide corresponding to the deutoxide.

I have repeated and varied these experiments with the view of obtaining the percyanide of copper, but always without success; I have, however, observed some well-marked combinations of protocyanide with the percyanide, which I now propose to describe.

Protopercyanide of Copper.—For the preparation of this compound, a diluted solution of cyanide of potassium or hydrocyanic acid must be poured into a solution, also diluted, of a salt of copper, in such a proportion as to leave a great excess of undecomposed copper salt in the liquid. It may also be obtained by passing a current of hydrocyanic acid through hydrated oxide of copper held in suspension in water; in these reactions a precipitate is formed, which is at first yellow, but passes rapidly into green, disengaging at the same time a considerable quantity of cyanogen.

The green precipitate thus obtained has a slightly crystalline appearance, and a constant composition. Analysis leads to the formula—

$$Cu^2 C^2 N, CuC^2 N, HO.$$

At 212° F. it loses its water without decomposition; a higher temperature converts it into protocyanide of copper, with evolution of cyanogen.

It dissolves very readily in cyanide of potassium; the liquid thus obtained, which is colourless or slightly bluish, soon forms a crystalline mass of a pearly lustre; it is protocyanide of copper and potassium which is formed in this reaction, with elimination of cyanogen.

Caustic potash converts protopercyanide of copper into oxide of copper and protocyanide of copper and potassium; acids separate from it the white protocyanide of copper, at the same time forming a copper salt, with disengagement of hydrocyanic acid.

Ammonia dissolves it readily, forming a blue liquid, from which spontaneous evaporation causes the deposition of fine green acicular crystals of biammoniacal protopercyanide of copper.

Double Protopercyanide of Copper.—When a solution of a salt of copper is precipitated by a tolerably concentrated solution of cyanide of potassium, employed in sufficient quantity to precipitate nearly all the copper, an amorphous powder, of an olive-yellow colour, is obtained, with abundant evolution of cyanogen; this substance has a constant composition, corresponding to the formula—

$$2(Cu^2 C^2 N)\, CuC^2 N, HO.$$

These two compounds of protocyanide of copper with the percyanide are rather unstable; they become converted into proto-

* Comptes Rendus, xix. p. 909.

cyanide of copper, with loss of cyanogen, either spontaneously or by the action of the slightest increase of temperature, or especially in the presence of an excess of hydrocyanic acid.

Ammoniacal Protopercyanide of Copper.—If cyanide of ammonium be substituted for cyanide of potassium in the precipitation of the salt of copper, an abundant evolution of cyanogen is also produced, but the bluish-green precipitate thus obtained always contains ammonia. Its analysis gives the formula—

$$Cu^2 C^2 N, CuC^2 N, NH^3, HO.$$

It presents the appearance of a bluish-green amorphous powder, which is slightly soluble in cold water; when boiled in this fluid, it becomes converted, with evolution of ammonia, into ammonio-protocyanide of copper, which remains in solution, and into protocyanide of copper, which is precipitated.

The protocyanide of copper obtained in this and some other analogous reactions, offers a more or less intense brown colour; its composition, however, is not altered. Its analysis gave the same numbers as that of the white protocyanide of copper.

The ammoniacal protopercyanide of copper undergoes no change in the air; at a temperature of 212° F. it loses water and ammonia; a little stronger heat rapidly converts it into protocyanide of copper.

Biammoniacal Protopercyanide of Copper.—The ammoniacal protopercyanide of copper dissolves very readily in ammonia, forming a liquid of a sky-blue colour, which deposits beautiful green acicular crystals by spontaneous evaporation. This new body consists of protopercyanide of copper combined with 2 equivs. of ammonia; its formula is—

$$Cu^2 C^2 N\, CuC^2 N, 2NH^3.$$

A much more convenient method of preparing this compound consists in passing a stream of hydrocyanic acid into oxide of copper, held in suspension by ammonia under the influence of hydrocyanic acid; the excess of oxide of copper first dissolves; small brilliant green acicular crystals then make their appearance in the liquid; the operation is stopped at this point, when the liquid deposits a fresh quantity of crystals on cooling.

This salt is also produced when protocyanide of copper is dissolved in ammonia. If this solution be prepared without contact of air, it is colourless; but as soon as it comes in contact with oxygen, it rapidly acquires a blue colour, and on evaporation deposits green acicular crystals of the preceding salt.

The biammoniacal protopercyanide of copper presents the appearance of beautiful green prismatic needles, with a metallic lustre. It undergoes no change in the air, is insoluble in water, and presents the same reactions with different tests as the protopercyanide and ammoniacal protopercyanide of copper.

Triammoniacal Protopercyanide of Copper.—The biammoniacal protopercyanide of copper dissolves very readily in ammonia by heat; and when this operation is effected, keeping constantly an excess of ammonia in the liquid by means of a current of this gas, the

solution on cooling deposits either prismatic needles or crystalline laminæ of a fine blue colour; this is triammoniacal protopercyanide of copper. Analysis gives the formula—

$$Cu^2\,C^2\,N\,CuC^2\,N, 3NH^3.$$

Exposed to the air, this salt loses ammonia, and becomes green. This salt may also be prepared from the protopercyanide and ammoniacal protopercyanide of copper.

Ammoniocyanide of Copper.—In the preparation of the biammoniacal protopercyanide of copper by means of hydrocyanic acid and oxide of copper held in suspension by ammonia, if the disengagement of gas be continued after the formation of the green crystals, these crystals first become redissolved, the fluid then grows paler by degrees, and soon loses its colour completely. By concentration and slow cooling, it deposits colourless, prismatic, acicular crystals of this salt. Their analysisgave the formula—

$$Cu^2\,C^2\,N\,NH^4\,C^2\,N.$$

It consequently corresponds with the potassiocyanide of copper, $Cu^2\,C^2\,N\,KC^2\,N$. No ammoniocyanide of copper corresponding with the salt $3(KC^2\,N)\,Cu^2\,C^2\,N$ appears to exist; at least my endeavours to prepare it have been unsuccessful.

This salt, like the corresponding copper salt, is but little soluble in water; like it, it is decomposed by long boiling in that liquid. Heated to 212° F., it loses cyanide of ammonium; a temperature a little higher is sufficient to convert it rapidly into pure protocyanide of copper.—*Comptes Rendus*, June 20, 1853, p. 1099.

Action of Phosphorus, Sulphur, Arsenic, and Antimony upon certain Classes of Salts. *By* J. W. Slater, Esq.*

I. *In the Moist Way.*

1. *Permanganates.*—A solution of the permanganate of potash is decomposed by phosphorus, pulverized metallic arsenic, antimony and sulphur at ordinary temperatures, as well as when boiled. The action of arsenic is almost instantaneous, probably from its minute subdivision and the angular form of the fragments. [The permanganate, it may be mentioned, is decomposed when boiled with angular bodies even of a kind which have no direct chemical action, such as pounded Berlin-ware.] Sulphur exerts a comparatively feeble action. The presence or absence of light has no apparent influence. With phosphorus the products are, after boiling, a brownish-black deposit of hydrous peroxide of manganese. The clear liquid, on concentration, yields long acicular crystals, containing phosphate and phosphite of potash. There is also a trace of phosphate of protoxide of manganese. In the cold the results are very similar; the liquid contains phosphate of potash, but no phosphite, whence in the former case the phosphorous acid was probably formed at the expense, not of the permanganic acid, but of the atmosphere during ebullition.

* Communicated by the Author.

With sulphur the results were sulphate of potash and hydrated peroxide of manganese.

With antimony, antimoniate of potash and hydrous peroxide.

Permanganate of potash is likewise decomposed when filtered over animal charcoal.

2. *Chromates.*—The yellow and red chromates of potash are both decomposed by phosphorus at ordinary temperatures. The products are phosphates of potash and a sediment of phosphate of chromic oxide. The liquid, however, even after the lapse of a year, still contained chromic acid, and had not lost its original colour. At a boiling temperature the decomposition may be completed. The liquid, if the bichromate has been employed, then assumes a green colour, and contains both phosphate and phosphite of potash. The green colour of the solution is due to the circumstance, that phosphate of chromic oxide is plentifully soluble in free phosphoric acid, as is likewise the arsenite of the same base in free arsenious acid.

With powdered metallic arsenic the results are analogous.

Sulphur does not decompose the chromates in the moist way.

The chromates of potash are not perceptibly decomposed, either when digested with animal charcoal, or with wood charcoal recently ignited and pulverized, or when a piece of red-hot charcoal is plunged into the solution.

Chromate of copper boiled with phosphorus is decomposed; there are formed metallic copper, black phosphide of copper and phosphate of chromic oxide. The supernatant liquid, which is green and very acid, contains phosphoric and phosphorous acids holding phosphate of chromic oxide in solution.

Chromate of lead, on boiling with phosphorus, is not perceptibly decomposed. The liquid contains free phosphoric and phosphorous acids, formed at the expense of the atmosphere. Aqueous phosphoric acid dissolves, even in the cold, a considerable quantity of chromate of lead, forming a pale yellow solution.

With metallic arsenic the results are similar. The liquid contains free arsenious acid.

3. *Chlorates.*—A solution of chlorate of potash, boiled with phosphorus, is decomposed; the liquid contains a mixture of phosphate and phosphite of potash, chloride of potassium and undecomposed chlorate; it has an acid reaction. With metallic arsenic the results are arseniate of potash and chloride of potassium.

4. *Nitrates.*—Phosphorus, boiled in a solution of nitrate of baryta, produces no decomposition. The slight precipitate formed consists of silica, the flask having been attacked.

Nitrate of baryta is decomposed by metallic arsenic after long boiling; arsenite of baryta is formed along with free arsenious acid.

Nitrate of lead, boiled with phosphorus, is decomposed, giving a white precipitate—phosphate of oxide of lead.

It is not decomposed when boiled with metallic arsenic.

Nitrate of copper, boiled with phosphorus, produces, if concentrated, a large quantity of cupric oxide and a little phosphide of copper. If dilute, metallic copper is deposited upon the phosphorus

even at ordinary temperatures, beneath which is found a large quantity of black phosphide, the liquid acquires an acid reaction, and contains free phosphoric acid.

Nitrate of copper, boiled with metallic arsenic, is decomposed, arsenite of cupric oxide being deposited.

II. *In the Dry Way.*

Fragments of phosphorus, carefully dried on bibulous paper, were sealed in a test-tube along with bichromate of potash, dried and finely powdered, and left in a dark place at the ordinary temperature. After some weeks, marks of decomposition became evident, the phosphorus being covered with a green crust of chromic phosphate. In the light no action was perceptible even after the lapse of fourteen months. Metallic arsenic had no action.

At higher temperatures the chromates are readily decomposed by phosphorus and arsenic, yielding a variety of products, which I have not yet found opportunity to examine.

Note on the Ozonization of the Oils of Lemon and Turpentine. *By* C. Greville Williams*.

In the Philosophical Magazine for June there was a short letter addressed to the Editors by me, "On a Method of distinguishing the Volatile Oils of the Series $C^5 H^4$."

Since that time I have made several experiments on the oils of turpentine and lemons, the results of which, I am in hopes, are likely to lead to a more complete investigation of this part of organic chemistry.

I have alluded in that letter to Schönbein's views of the nature of the principle which gives to some of the oils the power of converting the sulphuret into the sulphate of lead.

I have now found that distillation, or simply raising turpentine to its boiling-point for a short time, is sufficient to destroy its oxidizing property; but I failed to detect free oxygen in the air of the retort during ebullition.

On exposure to the air for twenty-four hours in an uncorked flask, the oil becomes again partially ozonized; and after forty-eight hours I found the power of discharging the colour from darkened lead-paper almost as strong as it was previous to the distillation.

It is very remarkable that the residue of the distillation, which was slightly yellow, had in this time acquired more than twice as much bleaching power as the colourless distillate.

I have strong reason to believe, from several of the phænomena which I have observed, that the ozone, instead of being liberated from the heated turpentine as gaseous oxygen, combines with it to form a resin, which remains behind in the distillation.

On this supposition, hydrogen ought to be liberated, but I have not detected it, and probably the quantity is too minute to be separated on the small scale in a state fit for examination; or, if ozone

* Communicated by the Author.

be O^2, it is possible that it may react in such a manner, that an equivalent of oxygen unites with the turpentine, and the other forms water with the hydrogen; and in support of this supposition I may adduce the fact, that on distilling the ozonized turpentine, the first portion came over cloudy from the presence of water.

It is important to observe, that oil of lemons, as pure as I have been able to obtain it, if exposed for a very considerable period to the atmosphere, acquires the power of discharging the colour from darkened lead-paper, though to a very slight extent compared with turpentine; and it results, in effect, that the difference in the behaviour of the two oils is only one of degree.

Laboratory, Oxford Court,
August 18, 1853.

Simple Means of Preventing the Formation of Incrustations in Boilers. *By* R. Fresenius.

It has been found, since 1851, that no incrustation was formed in the boiler of a steam-engine at Ems, whilst the water with which the boiler was supplied contained 21·899 grs. in the pound of solid matters. These were—

	grs.
Carbonate of soda	11·35488
Sulphate of soda	0·10790
Chloride of sodium	7·27020
Sulphate of potash	0·43653
Carbonate of lime	1·24370
Carbonate of baryta	1·06890
Carbonate of iron	0·01728
Carbonate of manganese	0·00868
Carbonate of baryta and strontian	0·00215
Phosphate of alumina	0·01090
Silica	0·37839
	21·89951

From this Fresenius concludes that it is not carbonate of lime, but only sulphate of lime which causes the formation of crust, and that in the present case this is prevented by the quantity of soda contained in the water. This has given occasion to investigations, in which soda was added to water containing sulphate of lime, which hitherto had always deposited incrustations. In these cases the action was always found successful, so that Fresenius regards the addition of soda as the simplest means for the prevention of incrustation.

The author gives the following rule to prevent the addition of soda in excess:—100 parts of anhydrous sulphate of lime are decomposed by 78 parts of pure calcined soda. The discovery of the correct quantity is so simple and easy, that this circumstance does not present the least difficulty. Care must be taken that there be always a slight excess of soda present, and the water in the boiler must therefore be tested from time to time. This is better and more

accurately effected than with test-paper, by dividing a sample (filtered if necessary) of the water of the boiler into two parts, and adding to one part solution of soda, to the other lime-water. If the former remains clear whilst the other is rendered slightly turbid, the proportion is correct. If the reverse is the case, soda must be added, whilst its quantity can be diminished if the turbidity with lime-water be very great.—*Journ. für Prakt. Chem.*, lviii. p. 65.

ANALYTICAL CHEMISTRY.

New and ready Method of determining the Alkalies in Minerals. PART II. *Conversion of the Sulphates into Chlorides: Qualitative Determination of the mixed Alkalies: Separation of the Alkaline Chlorides from each other, with a more direct Method of obtaining them from Silicates not soluble in Acids. By* J. LAWRENCE SMITH, Professor of Chemistry in the University of Virginia.

[Continued from page 259.]

Conversion of the Sulphates into Chlorides.

31. IN continuation of the subject, the next point to be considered is the conversion of the sulphates of the alkalies into chlorides. The method ordinarily adopted to accomplish this change is to precipitate the sulphuric acid by means of chloride of barium, care being taken to avoid the slightest excess of the latter. The annoyance attendant upon this exact precipitation is familiar to all who may have had occasion to make the trial.

32. Instead of the chloride of barium, the acetate of lead is used; a solution of this salt is poured in excess upon the solution of sulphates; warming the latter slightly, the sulphate of lead readily separates; the whole can be immediately thrown on a filter, and washed; a drop or two of the acetate of lead should be added to the filtrate, to ensure there being an excess of the lead salt.

33. The filtrate is then warmed, and sulphuretted hydrogen added; care must be taken to see that there is an excess of sulphuretted hydrogen, a test most readily performed by means of a piece of lead-paper. The liquid is thrown on a filter, to separate the sulphuret of lead; the filtrate containing the alkalies as acetates is evaporated, and when nearly dry, an excess of hydrochloric acid is added, and the whole evaporated to dryness over a water-bath, and finally heated to above 500°. A hot solution of the chloride of lead can be used instead of the acetate, rendering the addition of hydrochloric acid unnecessary.

34. It needs but little experience to convince one of the superiority of this method, over that by the chloride of barium, for converting the sulphates into the chlorides, its principal recommendation being the indifference with which an excess of the lead salt can

be added to precipitate the sulphuric acid, and the subsequent facility with which that excess of lead can be got rid of. It may be well to state, that experiments were made to prove the perfect precipitation of the sulphuric acid from the sulphates of the alkalies by salts of lead, and it is only after numerous comparative results that it is now recommended.

To distinguish the Alkalies from each other when mixed.

35. To distinguish potash, soda, and lithia when mixed, is attended with more or less difficulty according to the proportions in which they are mixed; of the three, potash is the most easily recognised, next in order is soda, and lastly lithia; the presence of which, mixed in small amount with proportionally large quantities of the other alkalies, it is almost impossible to determine with any accuracy without direct separation.

36. In the analysis of many minerals, the characters of which lead to the supposition of the presence of the alkalies, it is useless to precede the quantitative determination by one of a qualitative character, especially as the steps to be followed to separate the alkalies are the same in both cases, and to proceed in this way is œconomy of time. From my own experience concerning the constitution of the silicates, there are doubtless but very few of them without an appreciable quantity of alkalies in their constitution; and an easy method of examining with certainty the composition of such small quantities of alkaline chlorides must add to our analytical knowledge. With a little experience, the method about to be described will be found very available.

37. To ascertain the nature of the alkalies present in the chlorides before proceeding to separate them, we abstract a quantity so small as not sensibly to affect the weight of the mass. The smallest piece of the dried mass, that need not exceed $\frac{1}{50}$th of an inch in diameter, is placed on a slip of glass, and to it is added a drop of a watery solution of *very pure* chloride of platinum*, not too concentrated, and the plate gently warmed; if potash be present, a yellow deposit soon takes place, which by the microscope will be seen to consist of octahedral crystals of the double chloride of potash and platinum: the evaporation should be continued very gently with a heat not exceeding 120° to 130° until the liquid begins to dry on the edge; if this be now examined under the microscope, and soda be present, beautiful needle-shaped crystals will be seen, both formed and forming, with an oblique angle of termination, the crystals frequently having re-entering angles. The border of liquid on the glass is the place to observe these crystals, and that while the process of drying is going on. When the amount of soda is very small, it is best to allow the solution on the glass to dry in the slowest possible manner. Should the quantity of soda be still smaller or the nature of the crystals doubtful, resort may be had to polarized light, when the prismatic crystals of chloride of platinum and sodium will be at once rendered visible by their beautiful colours,

* The alcoholic solution does not give perfect results, and should not be used.

as they possess polarizing properties, whereas the crystals of chloride of platinum and potassium, besides differing in form, do not polarize light.

38. This method of detecting a small quantity of soda in the presence of potash I have employed since June 1850, while engaged in the examination of the collection of urinary calculi belonging to the Dupeytren museum at Paris; at that time it was employed daily in the laboratory of Messrs. Wurtz and Verdeil; the special reason for devising it was to examine the nature of the trace of alkali almost invariably found in the uric acid calculi after combustion.

39. The reason for making special reference to the date of the original employment of this method is to claim priority in its use, as Mr. Andrews announces it in a late number of the 'Chemical Gazette' as a new method. Were not the method so well known and so constantly employed in the laboratory of Messrs. Wurtz and Verdeil at the period above mentioned, I should not now set up any reclamation in the matter.

40. The amount of soda that can thus be detected is exceedingly small, as the liquid can be concentrated to the very smallest bulk. When the amount of potash is proportionally large compared with that of the soda, it is better to put the chloride of platinum in a drop of the solution of the alkaline chlorides placed in a watch-glass; allow the potash salt to settle, take a little of the clear liquid, place it on a slip of glass, evaporate slowly, and examine in the way already mentioned. We should avoid the use of alcohol as a solvent for the salts employed.

41. For the full appreciation of this method it requires some experience, and on first trials the extreme results will not be readily obtained; too much care cannot be taken with reference to the evaporation; sometimes, if the evaporation be a little too speedy, no indication of the presence of soda will be evinced; so, in all doubtful instances, the glass should be laid aside for an hour or two, when the excess of the chloride of platinum will attract moisture from the air, and afford an opportunity for the chloride of platinum and soda to crystallize regularly. For the most perfect success with very minute quantities of soda, too great an excess of chloride of platinum should be avoided. Those engaged in mineral analysis, who will employ this means of detecting the presence of the alkali, will find it of great assistance in facilitating their labours, especially when directed to very minute accuracy in their results, for I have reason to believe it rare to find in minerals any one of the alkalies perfectly free from one of the others.

42. When the chloride of lithium is present, it interferes materially with this method of detecting small amounts of soda; for owing to its very deliquescent nature, it abstracts moisture from the air, and dissolves the double chloride of sodium and platinum, or prevents altogether its formation in recognizable crystals. These investigations have added nothing to what is already known concerning the detection of lithia mixed with soda and potash; the plan invariably adopted is to treat the mixed chlorides with a solu-

tion of alcohol and æther, and examine the part dissolved by the blowpipe. Details as to the manner of using the alcohol and æther solution are given under the next head.

Separation of the Alkalies from each other.

43. Under this head I have nothing to add to what is already known on the subject: it may be well, however, to mention the manner in which Rammelsberg's method of separating lithia has been employed, as it has not yet been fairly tested in this country. His method, it is well known, is based on the solubility of the chloride of lithium in a mixture of equal parts of absolute alcohol and æther, neither of the other chlorides being dissolved by this menstruum. A number of experiments were made on known quantities of the alkalies, and the results of some of them are as follows:—

a. 500 milligrms. chloride of potassium, treated with the mixture of æther and alcohol, 10 grms. of the latter being used, yielded only $\frac{3}{10}$ths of a milligramme to the liquid.

b. 500 milligrms. of chloride of sodium, treated in the same way, yielded $\frac{1}{2}$ a milligramme to the liquid.

c. A mixture of chlorides of potassium, sodium and lithium, in which the latter constituted 2 per cent. of the mass, was acted on by the æther and alcohol, filtered and evaporated to dryness; the residue was equal to 2·53 per cent. The quantity used was KCl and NaCl each 200 milligrms., LiCl 0·8 milligrm.

d. A similar mixture, containing 18·10 per cent. of chloride of lithium, furnished a residue of 17·65 per cent.

e. A similar mixture, containing 67·20 per cent. chloride of lithium, gave a residue of 68·40.

44. By these results it may be seen that this method of separating lithia from the other alkalies may be perfectly relied on. It only remains to detail the precautions to be taken in order to ensure accurate results.

45. The solution of alcohol and æther must be made of absolute alcohol mixed with its volume of pure æther. The chlorides must be dried thoroughly at 212°, or a little above; if they have at any time been heated much higher, a drop or two of hydrochloric acid must be added to the chlorides, which are subsequently dried at the temperature just mentioned. The desiccation is best carried on in a small-sized capsule. To the dry mass, a small quantity of the mixture of alcohol and æther is added, and stirred with a small glass rod; the chlorides soon disintegrate; the capsule and its contents are placed on a glass plate, and covered with a small bell-glass; (a common tumbler answers the purpose very well, especially if the edge be ground;) this is left to digest for twenty-four hours, and then thrown on a filter, and washed with the *alcohol-æther* solution; the chlorides of sodium and potassium remain on the filter. These last can be dissolved off the filter by means of water, and separated in the ordinary way.

46. The alcohol-æther solution of chloride of lithium is evaporated to dryness, converted into sulphate, and weighed. The results

thus obtained far exceed in accuracy those from any other method for separating lithia. The indirect method, by ascertaining the quantity of sulphuric acid contained in the mixed sulphates, is the next best, but, like all indirect methods of analysis, should never be employed except when it is absolutely necessary.

47. When the alkalies are present in the form of chlorides before their quantity has been estimated in some other form, it is best to proceed first to the separation of lithia, afterwards weigh the chlorides not dissolved by the *alcohol-æther*, and lastly, separate the potash chloride from the soda chloride, if both be present, by means of the bichloride of platinum. Experiments were made with a mixture of alcohol and chloroform, the results of which were not so satisfactory as those afforded by the alcohol-æther.

Substitution of Chloride of Ammonium for Fluoride of Calcium, to mix with Carbonate of Lime for decomposing the Silicates.

48. It was mentioned in the previous paper on this subject how carbonate of lime could be rendered as powerful in its decomposing agency on the silicates as caustic potash, the effect being due to the use of some flux, fluoride and chloride of calcium being used for that purpose. I have since tested more carefully the merits of the chloride of calcium, and for various reasons prefer it to the exclusion of the fluoride. In the first place, it introduces chlorine instead of fluorine into the analysis; and secondly, the fused mass is more easily detached from the crucible, and dissolved by hydrochloric acid.

49. The manner of introducing the chloride of calcium into the mixture of mineral and carbonate of lime was a point of some little importance, as from the deliquescent nature of that compound it was inconvenient to weigh and mix it with the carbonate of lime and mineral; these difficulties are obviated by employing *chloride of ammonium* to form indirectly the chloride of calcium.

50. The process, which appears to leave hardly anything to desire, is to take 1 *part of the finely-pulverized mineral, 5 to 6 of carbonate of lime, and* $\frac{1}{2}$ *to* $\frac{3}{4}$*ths of chloride of ammonium**; mix them intimately in a glazed mortar, introduce the mixture in a platinum crucible, heat to bright redness in a furnace† from thirty to forty minutes.

51. There is no silicate, which, after having undergone this process, is not easily dissolved by hydrochloric acid. For the action of the lime to have been complete, it is not necessary that the mass should have settled down in perfect fusion. The contents of the

* The chloride of ammonium is best obtained in a pulverulent condition by dissolving some of the salt in hot water, and evaporating rapidly; the greater portion of the chloride of ammonium will deposit itself in a pulverulent condition, the water is poured off, and the salt thrown on bibulous paper allowed to dry; the final desiccation being carried on in a water-bath, or in any other way with a corresponding temperature.

† An ordinary portable furnace, with a conical sheet-iron cap of from 2 to 3 feet high, answers the purpose perfectly well, all the requisite heat being afforded by it.

crucible are dissolved, and the analysis continued as pointed out in 19, 20, 21, &c.

52. This method ensures the obtaining of every particle of the alkalies in the mineral examined, requiring no more precaution than any good analyst is expected to take in the simplest of his processes; and not the least of the advantages is the ready method of separating all the other ingredients and the small accumulation of water arising from the little washing necessary.

A more speedy method of separating the Alkalies directly from the Lime-fusion for both Qualitative and Quantitative Determination.

53. As soon as the fusion with carbonate of lime and sal-ammoniac gave evidence of the mineral being so thoroughly attacked, the question naturally arose as to the condition the alkalies were in after the fusion, and the possibility of dissolving them out by the agency of water alone, at least for the purpose of qualitative determination. Experiments directed to this object soon made it evident that the alkalies might be obtained from any silicate, without resorting to the use of acid as a solvent for the fusion.

54. The mass, as it comes from the crucible, is placed in a capsule with water, and then heated in a sand-bath or over a lamp for two or three hours, renewing the water from time to time as it evaporates. The mass disintegrates very shortly after being placed in the water. The contents of the capsule are next thrown on a filter, and the water passes through containing the chloride of the alkalies, a little chloride of calcium and caustic lime; all else that the mineral may have contained remains on the filter, except baryta and strontia, if they be present in the mineral; but as these oxides are of rare occurrence in silicates, no allusion will be made to them here.

55. To the filtrate add carbonate of ammonia, and boil for some time, when all the lime will be precipitated as carbonate; add a few drops of a solution of carbonate of ammonia to the hot solution, to be sure that all the lime is precipitated; should this be the case, filter; the filtrate will contain the chlorides of the alkalies and chloride of ammonium; it is evaporated to dryness over a water-bath in a small platinum capsule; the capsule is carefully heated to expel the sal-ammoniac, and finally heated to 700° or 800° F.; it is then weighed with its contents, and the chlorides, if mixed, separated in the way mentioned (45 and 46). The amount of sal-ammoniac to be expelled is quite small, not equalling the weight of mineral originally employed.

56. Nothing in analysis can be simpler or more speedy than this process. Its constant accuracy still lacked some little to render it perfect, as usually an amount of alkali remained behind, amounting to from $\frac{3}{10}$ths to 1 per cent. of the mineral used; certainly a small quantity, but still too much to be omitted in an accurate analysis. This also must be arrived at, and it can be accomplished in the following manner:—

57. After the fused mass has been treated with water, filtered and washed, as in (54), the filter and its contents are dried; the

latter are detached from the filter, and rubbed up in a glazed mortar with an amount of sal-ammoniac equal to one-half the weight of the mineral, and reheated in a platinum crucible exactly as in the first instance, treated with water, thrown on a filter and washed, the filtrate added to that from the first fusion, the whole treated with carbonate of ammonia, and completed as in (*55*).

58. This second fusion complicates the method but little, as the residue on the filter readily dries in a water-bath into a powder that is easily detached from the filter; and the small portion adhering to the latter may be disregarded, as the alkalies remaining rarely exceed more than $\frac{1}{500}$th of the whole mass, and in most instances not more than $\frac{1}{1000}$th. In many analyses made, one fusion sufficed for the entire extraction of the alkalies; but as a few tenths would occasionally remain behind, we preferred the additional fusion to get at that small quantity, and to entitle it to rank as a method by which all but the merest trace of the alkalies could be extracted from the insoluble silicates.

59. The proportion of sal-ammoniac added to the carbonate of lime as here recommended, was arrived at after numerous experiments. By increasing the sal-ammoniac, and thereby augmenting the amount of chloride of calcium formed, the mass fuses more thoroughly, but the water does not disintegrate it as completely as when the ammoniacal salt is less; also the accumulation of this latter at the end of the process is less,—an object not to be disregarded. The advantage of thus estimating the alkalies in insoluble silicates is obvious; the long routine of separating silica, alumina, lime, &c., is done away with; the accumulation of chloride of ammonium is very trifling; and lastly, the alkalies are obtained directly in the form of chlorides. The method will vie in accuracy with any other, including the one already mentioned in the first part of this paper, and at the same time it is unequalled in simplicity, speed of execution and constancy of results.

60. In examining for alkalies qualitatively, one fusion will of course be all that is necessary, and the action of the water need not be continued more than thirty minutes before filtering. This method will not answer when boracic acid is present in the silicate; the manner of proceeding in such a case will be mentioned in a future paper on the determination of boracic acid in minerals.

61. There is nothing new in the attempt to dissolve out the alkalies by water from a silicate that has been heated with lime. M. Fuchs used the method for procuring lithia from lepidolite; but of course his efforts were entirely directed to procuring the lithia from the mineral, and not to estimating its quantity, as the method he followed could not have furnished such results. I have also lately learned that Mr. A. A. Hayes, of Boston, proposed and employed a mixture of chloride of calcium and caustic lime, to decompose alkaline silicates, heating over a lamp, and subsequently treating the mass with water to extract the alkalies or chlorides: as little has been heard of this process, I presume the author found it defective. If we are correctly informed, the proportions used were 3 parts of

chloride of calcium and 1 of caustic lime: experience proves that however readily such a mixture may reduce the felspars, it fails when tried on kyanite, zircon, micas, and other silicates difficult of decomposition. This arises from the fact that the chloride of calcium has but little decomposing effect on the silicates, its action being simply that of a menstruum in which the lime can act conveniently on the mineral.

62. The use of lime or its carbonate mixed with chloride of calcium or chloride of ammonium, for the purpose of effecting the decompositions alluded to, would be considered by me of questionable utility if the mixture were not so proportioned and employed as to decompose the most difficult silicates if necessary; for unless this be done, we can at no time be certain that the decomposition is complete. As a general rule for decomposing silicates by lime or soda, it is far better to use a charcoal fire than the flame of a lamp, as it is better to heat too high than not to heat sufficiently the mineral to be acted on.

Complete Analysis of an Insoluble Silicate on one portion of the Mineral.

63. The attempt to accomplish an analysis of this description deserves no encouragement, from the almost invariable inaccuracy attending the results. If we have a given quantity of any one of the silicates alluded to, requiring analysis, we had better subdivide it, however small the entire quantity may be, ascertain one set of ingredients by the soda, and the other by the lime-fusion; for the results thus obtained may be relied on as more accurate than those furnished by an analysis of the whole quantity through the agency of baryta or hydrofluoric acid.

64. Should it be desired to undertake the analysis on a single portion, I would recommend the silicate to be attacked with *carbonate of baryta mixed with the chloride*,—3 to 4 parts of carbonate and 2 of chloride. This mixture can be made to decompose all silicates at a much lower temperature than when the carbonate alone is used, but its action is not near so powerful as the carbonate of lime and sal-ammoniac.

65. This terminates an account of my labours in the determination of the alkalies in insoluble silicates; the conclusions have been arrived at from more than two years' experience, and over a hundred alkali determinations by myself and others, made on minerals of the most varied composition. In my laboratory, an accurate alkali determination is one of the most simple and speedy analytical processes now conducted, and the presence of magnesia in no degree complicates the result. A little experience will no doubt bring others to the same conclusions. Many singular decompositions of salts have been noticed in the course of these researches; but as they do not bear directly on the object of this article, they will be made known on some other occasion.

Many analytical processes mentioned in this article can be applied when operating on soluble silicates.—Silliman's *Journal*, July 1853.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Examination of Acetone. *By* Prof. G. STÆDELER.

MANY organic acids, especially those belonging to the series $C^n H^n O^4$, split, when their combinations with alkalies or alkaline earths are submitted to distillation, into carbonic acid salts and peculiar substances with a neutral reaction, which are partly fluid and partly solid; these are distinguished from the original acids only by containing 1 atom of carbon and 2 atoms of oxygen less. Of the substances here referred to *acetone* has been the longest and best known; it is to be regarded as the prototype of the whole group, which is on this account usually characterized by the name of acetones or ketones.

Acetone has frequently been the subject of chemical investigation; a great number of its products of decomposition have been made known, but the principal point, and that for the solution of which most of the investigations have been instituted, namely, what arrangement of atoms was to be accepted for acetone, has not hitherto been satisfactorily settled.

Kane arrived at the conclusion, that it ought to be ranged amongst the alcohols; and his view has acquired some weight, principally because it was acceded to by Berzelius. The author proves however that Kane's opinion is quite untenable, and that even the behaviour of acetone with sulphuric acid only presents an apparent analogy with the process of the formation of æther.

The author succeeded in producing from acetone a series of compounds and products of substitution, which, it appears, leaves no further doubt as to its constitution. In its behaviour in combination and decomposition, it exhibits the greatest affinity with the aldehydes, and especially with oil of bitter almonds. Like this, it forms a conjugate formic acid, which is homologous with lactic and formobenzoilic acids; with ammonia it is converted into an organic base, which comes next to amarine; and by the simultaneous action of ammonia and sulphuret of carbon or sulphuretted hydrogen, it furnishes interesting bases containing sulphur. Of the products of substitution of acetone containing chlorine, only a bichlorinated acetone was formerly known; but, as it appears from the following investigation, the whole of the hydrogen of the acetone can be exchanged for chlorine. These products containing chlorine not only result

directly from acetone, but also from many other organic substances. They are obtained from kinic, gallic, citric, salicylic and catechuic acids, flesh, starch, sugar, &c., when they are submitted to distillation with muriatic acid and chlorate of potash, or with muriatic acid and peroxide of manganese. The formation of acetone by the oxidation of caseine, albumen, fibrine, gelatine and gluten, stands in unmistakeable connexion with these facts. Acetone makes its appearance here in company with various aldehydes and their corresponding acids. Amongst the products of oxidation we find benzoic acid and oil of bitter almonds, valerianic acid and the aldehyde of valerianic acid, butyric acid and its aldehyde, acetic acid and common aldehyde. As acetone has the same composition as the aldehyde of propionic acid, which also occurs amongst the products of oxidation, it might be supposed that this acid would result from the oxidation of acetone; and on this point the author has ascertained that propionic acid is really formed by the not too violent action of oxidizing materials upon acetone. Nevertheless acetone cannot be regarded as the aldehyde of propionic acid, for its boiling-point, its behaviour with finely-divided platinum and oxygen, and the circumstance that the whole of its hydrogen may be displaced by chlorine, contradict this view completely.

If acetic acid be regarded as a methyle compound, namely, as formic acid in which 1 equiv. hydrogen is replaced by 1 equiv. methyle $=C^2\left\{\begin{matrix}H\\C^2H^3\end{matrix}\right\}O^4$, the formula of acetate of potash is $=C^2\left\{\begin{matrix}K\\C^2H^3\end{matrix}\right\}O^4$; and the decomposition which this salt undergoes by heat might be explained by the following formulæ:—

$$C^2\left\{\begin{matrix}K\\C^2H^3\end{matrix}\right\}O^4 = 2CO^2 + K, C^2H^3K, C^2H^3 + C^2\left\{\begin{matrix}K\\C^2H^3\end{matrix}\right\}O^4$$
$$= 2KO + C^2\left\{\begin{matrix}C^2H^3\\C^2H^3\end{matrix}\right\}O^2.$$

There would therefore originate in the first place carbonic acid and methylide of potassium,—a compound analogous to methylide of zinc,—which would become converted with a second atom of the acetate into potash and acetone.

As the composition of the aldehyde, according to the above symbolization, must be expressed by the formula $C^2\left\{\begin{matrix}H\\C^2H^3\end{matrix}\right\}O^2$, acetone would have to be regarded as ordinary aldehyde in which the basic equivalent of hydrogen has been replaced by methyle, *i. e.* as hypoacetylite of oxide of methyle.

With this admission, the author finds no contradiction in any of the reactions of acetone. Just as the cyanic æthers agree exactly with the pure acid in their behaviour towards ammonia, acetone, the methylic æther of aldehyde, bears the essential character of the latter. It exists in polymeric, and no doubt also in metameric modifications, for the occurrence of propionic acid amongst the products of oxidation of acetone points distinctly to this. The author

regards xylite, the formula for which is most probably $C^{18} H^{18} O^6$, as a polymeric modification of acetone; and Kane's mesitylene and oxide of mesityle must be regarded as products of the decomposition of this polymeric modification.

The following combinations, with the investigation of which the author has principally occupied himself, support the opinion just expressed upon the constitution of acetone:—

a. Products of Substitution containing Chlorine.—These are obtained by the introduction of chlorate of potash into a mixture of acetone and tolerably concentrated muriatic acid; they separate in a short time in heavy oleiform drops. The less chlorine they contain, the more insupportable is their odour, and the more violent the inflammation which they produce when brought into contact with the skin. The products which are poorer in chlorine are decomposed by potash, with the production of a brown colour and separation of resinous masses, whilst the addition of potash to those which are richer in chlorine effects no change in the colour. The compounds act in the same manner with concentrated sulphuric acid. They are remarkably characterized by the fact, that they are much more abundantly soluble in cold than in hot water; a saturated cold solution becomes turbid even with the warmth of the hand, whilst a heat of 122°–140° F. separates the greater part of the compounds in heavy colourless drops. The author has already made known the fact, that oleaginous bodies, which exhibit the same remarkable behaviour, are produced by the decomposition of many organic substances by nascent chlorine; he has now ascertained also that these do not differ in composition from the acetone products of substitution containing chlorine. They are obtained in most abundance when kinic acid, citric acid, or gallic acid are submitted to distillation with muriatic acid and chlorate of potash. Without the aid of the sunlight, however, more than 5 equivs. of hydrogen are not exchanged for chlorine.

Pentachlorinated Acetone, $C^2 \left\{ \begin{matrix} C^2 & Cl^3 \\ C^2 H & Cl^2 \end{matrix} \right\} O^2$, is a tolerably mobile colourless fluid, of a burning aromatic taste, and a peculiar odour similar to that of chloral. It does not solidify at −4° F., becomes gradually volatilized in the air, and boils at about 374° F.; its spec. grav. is between 1·6 and 1·7. With 8 equivs. of water it forms a compound, which crystallizes in rhombic tables, and fuses at about 61° F. Its watery solution has a distinct acid reaction. The formula above given is confirmed by the decompositions observed.

Hexachlorinated Acetone, $C^2 \left\{ \begin{matrix} C^2 Cl^3 \\ C^2 Cl^3 \end{matrix} \right\} O^2$, is obtained from citric acid by decomposition with chlorine gas, with the assistance of the light of the sun. It resembles the preceding compound in every respect; with 2 equivs. of water it forms a crystalline hydrate, which fuses at 59°–61° F. Plantamour, who discovered this compound, gave the formula $C^8 Cl^8 O^3$ for it; the author, however, shows that its composition agrees equally well with the formula above given.

b. Acetonine.—A solution of ammonia in acetone, exposed to spontaneous evaporation, leaves behind a colourless syrup-like residue, which does not crystallize by exposure to great cold. It is soluble in water, alcohol and æther, does not become brown by boiling with potash, and reduces silver salts in the same manner as aldehyde-ammonia. When kept, the compound gradually passes by spontaneous decomposition into an organic base, which the author calls acetonine. The formation of the base is more rapidly effected when acetone saturated with ammonia is heated to 212° F. in a hermetically-sealed tube. Its composition agrees with the formula $C^{18} H^{18} N^2$; it consequently stands in the same relation to acetone as amarine to oil of bitter almonds; and it may be supposed that the compound preceding the acetonine has a composition analogous to that of hydrobenzamide, and that it therefore contains the same elements in the same proportions as acetonine. In consequence of its ready decomposability, an analysis was not possible.

Pure acetonine is a colourless fluid, with an alkaline reaction, of a peculiar, somewhat urinous odour, and a burning taste. It dissolves readily in æther, in alcohol, and also in water; the addition of potash to its watery solution causes it to separate again in oleiform drops. Watery acetonine acquires a milky turbidity throughout on the application of a gentle heat, like watery coniine. Its platinum compound, $C^{18} H^{19} N^2 Cl + PtCl^2$, crystallizes in orange-yellow, shining, four-sided prisms, with oblique terminal faces. It is insoluble in æther, but soluble in water and in boiling alcohol to which some muriatic acid has been added. Binoxalate of acetonine, $C^{18} H^{18} N^2$, HO, $C^2 O^3 + HO$, $C^2 O^3 + 2HO$, crystallizes from its boiling saturated alcoholic solution in delicate white prisms, which are readily soluble in water, but not in æther. At 212° F. it loses 1 equiv. of water, and is decomposed by a somewhat stronger heat.

c. Carbothiacetonine and Thiacetonine.—From a mixture of acetone, sulphuret of carbon and ammonia, a compound is slowly deposited in yellowish crystals, for which Hlasiwetz has given the very improbable formula $C^{30} H^{26} N^3 S^9$. By the consideration of the decomposition which sulphuret of carbon undergoes by the action of liquid ammonia, we arrive at another formula, which agrees pretty well with Hlasiwetz's analyses. The compound is the hydrosulphate of an organic base containing sulphur, *carbothiacetonine*, $C^{20} H^{18} N^2 S^4$, for the formation of which 3 equivs. of acetone are decomposed by 2 equivs. of sulphocarburet of ammonium: as in the action of ammonia upon acetone, 6 equivs. of water are produced. The author shows that the platinum compound produced from the hydrosulphate of carbothiacetonine must have the formula $C^{20} H^{18} N^2 S^4, PtS^2 + PlCl^2$, and that the mercurial precipitate investigated by Hlasiwetz ($C^{30} H^{26} N^3 S^9 + 27HgS + 18HgCl$) was nothing but $HgCl + 2HgS$, to which a small quantity of muriate of carbothiacetonine adhered.

By the simultaneous action of ammonia and sulphuretted hydrogen upon acetone, a sulpho-base is obtained, which the author calls *thiacetonine*, because it is formed from acetone in the same manner as thialdine from aldehyde. The composition of thiacetonine is

probably expressed by the formula $C^{18}H^{19}NS^4$. It appears to be identical with Zeise's akcethine, which he obtained with many other products by the introduction of sulphur into anhydrous acetone which had been previously saturated with ammonia. It crystallized in very shining yellowish rhombohedra; it had an alkaline reaction, and dissolved readily in dilute acids, æther, alcohol and acetone, but was rather difficult of solution in water. It had consequently a resemblance to thialdine. The same compound appears also to be produced by boiling an alcoholic solution of hydrosulphate of carbothiacetonine, $C^{20}H^{18}N^2S^4, 2HS + 4HO = C^{18}H^{19}NS^4 + (NH^3 + 2CO^2 + 2HS)$.

d. Acetonic Acid, $C^8H^8O^6 = HO, C^8H^7O^5$.—This is produced from acetone in the same manner as formobenzoilic acid from oil of bitter almonds. It crystallizes in prisms, has a strongly acid taste and reaction, dissolves readily in water, alcohol and æther, and fuses when heated into a colourless oily fluid, which again solidifies in a crystalline form on cooling. By fusion with an excess of hydrate of potash, it produces acetone; when heated with concentrated sulphuric acid, it is decomposed with an abundant evolution of gas. It forms crystallizable salts with bases. The zinc salt, $ZnO, C^8H^7O^5 + 2HO$, is exactly like lactate of zinc, but only dissolves sparingly even in boiling water. It is insoluble in alcohol and æther. Its water of crystallization is expelled at a temperature a little above 212° F. The baryta salt, $BaO, C^8H^7O^5$, is readily soluble in water and alcohol, but insoluble in æther. It only crystallizes when the solution is very concentrated, forming small white prisms, or long fibrous, satin-like crystalline masses, which lose their water of crystallization even *in vacuo*. No compound could be formed with oxide of silver. On the addition of nitrate of silver to a tolerably concentrated solution of the acid neutralized with ammonia, metallic silver was slowly deposited in dark flakes.

The decomposition of acetone by means of hydrocyanic and muriatic acids did not furnish a base similar to alanine.

In the series of conjugate formic acids, the composition of which may be expressed by the general formula $C^nH^nO^6$, four acids are now known, namely glycic acid (homolactic acid), $C^4H^4O^6$; lactic acid, $C^6H^6O^6$; acetonic acid, $C^8H^8O^6$; and leucic acid, $C^{12}H^{12}O^6$; and it may be foreseen that their number will rapidly increase, as the material for their formation is furnished not only by the aldehydes, sugars, and some bases belonging to animal chemistry, but also by the ketones. It is even probable that two groups of acids exist, the composition of which may be expressed by the above formula. The aldehyde of propionic acid, for instance, must furnish an acid having the same composition as acetonic acid; the first however would agree with the formula $C^2H^2O^4, C^2\left\{\begin{matrix}H\\C^4H^5\end{matrix}\right\}O^2$, whilst the formula of the latter must be written $C^2H^2O^4, C^2\left\{\begin{matrix}C^2H^3\\C^2H^3\end{matrix}\right\}O^2$. There might consequently be an essential difference between the two acids. The author regards it as not im-

probable that the cause of the difference between ordinary lactic acid and that obtained from the juice of the flesh is to be sought for in some such relation; the conjunct in the one might be acetyle-aldehyde, $C^2 \left\{ \begin{matrix} H \\ C^2 H^3 \end{matrix} \right\} O^2$; that in the other the methyle compound of the formyle-aldehyde, $C^2 \left\{ \begin{matrix} C^2 H^3 \\ H \end{matrix} \right\} O^2$. For the solution of this question, important materials would be furnished by a careful comparison of the conjugate acids which might be produced from the aldehyde of butyric acid and from butyral as well as from œnanthole and butyrone.

It scarcely needs to be particularly stated, that the author regards, not only acetone, but the whole group of ketones, as æther-like compounds. According to his view, propione is $C^2 \left\{ \begin{matrix} C^4 H^5 \\ C^4 H^5 \end{matrix} \right\} O^2$, butyrone $C^2 \left\{ \begin{matrix} C^6 H^7 \\ C^6 H^7 \end{matrix} \right\} O^2$, valerone $C^2 \left\{ \begin{matrix} C^8 H^9 \\ C^8 H^9 \end{matrix} \right\} O^2$, and so forth; and for butyral he considers the probable formula to be $C^2 \left\{ \begin{matrix} C^2 H^3 \\ C^2 H^3 \end{matrix} \right\} O^2$. —*Nachr. von der Gesellsch. d. Wiss. zu Göttingen*, 1853, No. 9, p. 121.

On the Products of the Decomposition of certain Horny Substances. *By* A. C. Leyer *and* Köller.

The authors have treated feathers, hedgehog's spines, hair, globuline, hæmatine, and the elytra of the cockchafer with diluted sulphuric acid, and investigated their products of decomposition.

1 lb. of goose-feathers, which had been freed from dirt and fat by washing, was treated with 4 lbs. of sulphuric acid which had been previously diluted with 12 lbs. of water, and allowed to boil in a spacious glass vessel on the sand-bath. After the hot dilute sulphuric acid had acted upon the feathers for three hours, they swelled up, acquired a gelatinous appearance, and after boiling some time longer dissolved completely into a dark brown fluid. This fluid was kept at a boiling heat for four days, replacing the water driven off by fresh water. To remove the sulphuric acid, diluted milk of lime was now added to the fluid until it had a strong alkaline reaction; it was then boiled for a short time and filtered.

During the neutralization with milk of lime and the subsequent boiling, ammonia was evolved, together with a peculiar odour, which resembled that of the bases discovered by Wurtz. The filtrate was introduced into a retort for the purpose of distillation; the retort was then united with a Liebig's refrigeratory apparatus, in such a manner that the less volatile products could return into the retort; a vessel partially filled with dilute muriatic acid was then attached. The distillate was evaporated on the water-bath, completely dried, and then decocted with absolute alcohol; the alcoholic solution was again evaporated, and the extraction with alcohol repeated. The

mass of salts thus obtained became moist when exposed to the air for a short time, dissolved readily in water; and when evaporated on the water-bath with chloride of platinum, furnished crystals of a dark yellow colour, which dissolved partially in hot water. The amount of platinum contained in them was repeatedly determined; the quantity found was from 43 to nearly 44 per cent. Whether a small quantity of another ammonia base was present consequently remained undetermined.

After the evolution of ammonia had ceased, sulphuric acid was added to the fluid to throw down the excess of lime; to the filtrate from the precipitate thus produced acetate of lead was added as long as a precipitate was formed. The fluid was boiled for a short time with the lead precipitate and filtered; sulphuretted hydrogen was then passed through the filtrate to remove the excess of oxide of lead. The fluid filtered from the sulphuret of lead furnished, on evaporation and subsequent long standing, acicular crystals, grouped concentrically, which were obtained perfectly white by two crystallizations from water. Both the external characters and the analysis of these crystals show that they consist of *tyrosine*, $C^{18}\,H^{11}\,NO^6$.

The mother-liquor of the tyrosine still contained leucine and inorganic salts. For the preparation of the former, the following method was found to be the simplest and most rapid:—

To the mother-liquor a large quantity of strong alcohol is added, by which all the inorganic salts are thrown down; the filtrate is then evaporated, when the leucine crystallizes from it in quantity, and may be obtained perfectly pure by a single recrystallization from alcohol. It forms pearly laminæ, which fall to powder in every direction on being touched with a dry glass rod, are capable of sublimation, and when burnt diffuse an odour like that of roast fowls. The crystals dissolve readily in water, alcohol, acids and alkalies; analysis gave results agreeing exactly with leucine.

The authors have treated hedgehog's spines, human hair, and the elytra of the cockchafer in the same manner; and all these substances gave tyrosine and leucine.

The beards of feathers, put into glass tubes with water, closed up by fusion, and heated to 392° F., dissolved completely into a pale yellowish fluid, which had an odour of burnt feathers; in this a flocculent precipitate was deposited.

Globuline and Hæmatine.—Half a pailful of bullock's blood was left to coagulate spontaneously, the serum thus separated poured away, and the coagulum washed repeatedly with cold water. It was then divided into portions, tied up in linen cloths, and pressed under water. The red fluid thus obtained was repeatedly filtered through fine cloths to get rid of the small flakes of fibrine, and then coagulated by boiling with an addition of acetic acid. The coagulum thus obtained could only contain small quantities of albumen and fibrine, and must consist principally of what is usually characterized as blood-corpuscles. It was extracted with alcohol to which sulphuric acid had been added; this dissolved the hæmatine, whilst the globuline remained undissolved. The alcoholic solution, after neutraliza-

tion with ammonia, was evaporated to dryness, and the sulphate of ammonia separated from the hæmatine (which is insoluble in water) by washing the residue with water.

Both the globuline and hæmatine furnished an abundance of tyrosine and leucine by treatment with dilute sulphuric acid. For operating with a considerable quantity of globuline, the following method was employed:—

1 lb. of globuline was boiled for forty hours with 4 lbs. of sulphuric acid and 12 lbs. of water, milk of lime added to the brown solution thus formed, and the whole again heated. Sulphuric acid was added to the filtrate from the precipitate thus obtained until it only retained a weak alkaline reaction; the fluid was then filtered and evaporated. By this means the tyrosine crystallized in masses, and large quantities of leucine were also obtained from the mother-liquor of the tyrosine by the process above described. Free alkali is consequently not so hurtful to the crystallization as the free acid, which is present in the fluid in the form of sulphuric or acetic acid in every other mode of preparation. Besides, by this method the precipitation of the free sulphuric acid by acetate of lead is avoided, and this always carries down with it a considerable quantity of tyrosine and leucine. Independently of its simplicity, this method presents the advantage, that such frequent filtration is not necessary; for every precipitate, whether it consists of sulphate of lime, sulphate of lead or sulphuret of lead, encloses a portion of the crystallizable substance, which of course is a loss, as it is difficult to separate it from the precipitate.

Whether we admit that the blood-corpuscles contain as their chief constituents fibrine and albumen united with the colouring matter of the blood, or that they consist of the so-called globuline and hæmatine, the fact that the blood-corpuscles contain albuminous substances, similar to fibrine, caseine, albumen and horn-substance, is confirmed by this investigation; for the blood-corpuscles, by boiling with diluted sulphuric acid, furnish the same products of decomposition as the albuminous substances, which have already been examined in this respect.

According to the preceding observations, therefore, albumen, fibrine, caseine, horn, feathers, hair, the blood-corpuscles, and the elytra of cockchafers furnish tyrosine and leucine as products of their decomposition by treatment with dilute sulphuric acid.—*Journ. für Prakt. Chem.*, lviii. p. 273.

On two new Double Salts of Phosphoric and Molybdic Acid. *By* Dr. F. E. Zenker.

Fluids containing phosphoric acid give a yellow precipitate on the addition of a solution of molybdate of ammonia in muriatic acid. If this precipitate be dissolved in ammonia, the fluid first becomes blue, and afterwards colourless. From this fluid crystals of a new double salt are deposited, and afterwards usually crystals of molybdate of ammonia. The same salt is obtained directly by dissolving

together crystallized molybdate of ammonia and a small quantity of phosphate of ammonia, and allowing the salt to crystallize. The first that crystallizes is the

New Salt, $2NH^4O, 5MoO^3, 5HO + NH^4O, PO^5, 2HO$.—It generally appears in fan-like or sheaf-like groups of thin columnar or acicular crystals, which apparently belong to the triclinometric system. They dissolve readily in hot water, but are less soluble in cold; their solution has a slight acid reaction; if it be boiled, or merely exposed for a considerable time to the action of the air at a moderate temperature, ammonia disappears, and a white precipitate, which adheres to the sides of the vessel, is deposited; this is redissolved on the addition of ammonia. [Heat is consequently to be avoided in the preparation of the salt; the crystals may be readily recrystallized; they are dissolved in a little hot water with the addition of a few drops of ammonia; if the crystals be heated with the solution, it soon becomes turbid, and ammonia escapes.] If the crystals be exposed to the air whilst damp, they soon become somewhat dull, and are then only partially soluble, leaving a white pulverulent residue; when dry, they undergo no observable change either in closed vessels or in dry air. If muriatic or nitric acid be poured over them, they become converted, especially with the aid of heat, into a yellow powder; their watery solution also, when these acids are added to it, gives a yellow pulverulent precipitate. At a red heat they are converted into a bluish-gray or nearly black mass, which is only yellow in spots, and when heated with nitric acid becomes only partially yellow. Analysis:—

MoO^3	62·64	5	62·10
PO^5	12·58	1	13·83
NH^4O	13·50	3	12·79
HO	11·28	7	11·18

A potash double salt was obtained by the author by evaporating a solution of molybdic acid and a little phosphoric acid in muriatic acid to the consistence of a syrup, and saturating it with potash. The fluid set into a mass of scaly crystals, which resembled those of boracic acid. The crystals are colourless and glassy, and do not change in the air; they appear to belong to the monoclinohedric system; the most prevalent form is the clinopinacoid, and the vertical prism as well as the two hemipyramids; the crystals are tabular or columnar; the author proposes to give the measurement and more exact description hereafter. Their watery solution has an acid reaction; an addition of muriatic or nitric acid to the solution gives a yellow precipitate; the crystals also, when moistened with acid, acquire a yellow colour; when heated, they fuse readily with loss of water, forming a glass, which is yellowish when hot, and colourless and cracked when cold. Analysis:—

KO	17·77	4	17·96
HO	14·50	17	14·58
PO^5	7·24	1	6·88
MoO^3	60·49	9	60·58

Journ. für Prakt. Chem., lviii. p. 257.

Upon Selenæthyle. By C. A. Joy.

According to the recent investigations of Wöhler and Mallet upon telluric æthyle *, this substance behaves like an organic radical. From the great similarity existing between tellurium and selenium, it appeared very probable that the selenæthyle, discovered by Löwig in 1836, might behave in the same manner.

I have instituted some experiments on this subject in Prof. Wöhler's laboratory, at his desire, which however I am unfortunately compelled to leave unfinished, as I was unable to overcome the nausea which the odour of the selenæthyle produced. These experiments however, imperfect though they be, appear to me to be sufficiently decisive to prove that selenæthyle also possesses the properties of an organic radical.

Löwig obtained selenæthyle by the distillation of dry seleniuret of potassium with oxalic æther. I have preferred preparing it by the distillation of a solution of seleniuret of potassium with sulphoæthylate of potash.

For the preparation of the seleniuret of potassium, hydrate of potash was dissolved in 4 parts of water, the solution divided into two equal parts, one of which was completely saturated with seleniuretted hydrogen gas, so as to convert it into KSe+HSe, and then added to the other half.

The seleniuretted hydrogen gas was evolved by muriatic acid from seleniuret of iron, prepared by heating a mixture of equal parts of pure iron filings and powdered selenium in a glass retort. The formation of the seleniuret of iron takes place instantaneously, and is accompanied by fire, as already stated by Berzelius.

The evolution of the gas was effected in an apparatus from which all air had been carefully expelled by hydrogen, as it is immediately decomposed by contact with the air. It was retained in connexion with the apparatus for the evolution of the hydrogen gas, so that when the evolution of the seleniuretted hydrogen gas, which towards the end was assisted by heat, was finished, the latter gas could be completely expelled, and passed into the solution of potash, which was also in a vessel filled with hydrogen gas.

The solution of seleniuret of potassium thus prepared was mixed with a concentrated solution of sulphoæthylate of potash in a flask provided with a refrigeratory tube, and rapidly distilled as long as drops of selenæthyle passed over with the water. To every part of selenium employed, 2 parts of hydrate of potash and 4 parts of the sulphoæthylate were required. In this manner I procured about 25 grms. of selenæthyle.

It is a clear, pale yellow fluid, of an abominable odour, much heavier than water, and not miscible with it; when inflamed, it burns with evolution of red vapours of selenium.

Nitrate of Selenæthyle.—This is produced, with evolution of nitrous oxide gas, by the solution of selenæthyle in heated nitric

* Chem. Gaz., vol. x. p. 17, and vol. xi. p. 49.

acid of moderate strength. I did not succeed in obtaining it in the solid form, but only in that of a concentrated solution, which when further evaporated began to decompose. That it really contained nitrate of selenæthyle is shown by the following behaviour.

Chloride of Selenæthyle, $C^4 H^5 SeCl$.—The solution of selenæthyle in nitric acid behaves towards muriatic acid exactly like that of telluræthyle; on the addition of the latter acid, it becomes milk-white, and immediately afterwards drops of an oleiform body are separated. This is chloride of selenæthyle. It is a clear, pale yellow fluid, which sinks in water, and in the pure state appears to possess no smell. It is somewhat soluble both in water and in muriatic acid, which renders some care necessary in its preparation.

The determination of the chlorine was sufficient to prove the above formula. 0·438 grm. of the substance was decomposed in the usual manner by incandescent lime; by these means 0·600 grm. of chloride of silver was obtained, corresponding to 33·87 per cent. The formula requires 34·9 per cent.

The greater part of the chloride of selenæthyle was left for a considerable time in contact with the fluid containing nitric and muriatic acids, from which it had been formed. After a time, clear, colourless, very sharp crystals, of a large size considering the small quantity of fluid, were formed on the limit between the chloride and the supernatant fluid. I have not been able to ascertain what this substance may be; I can only say, that, to judge from its decomposition by heat and an elementary analysis, it is an organic compound of chlorine and selenium. The probable supposition that it might be a hydrate of chloride of selenæthyle could not be proved. Moreover, I could not produce it voluntarily by the solution of chloride of selenæthyle in water, or by any other means. It is readily soluble in water and alcohol, and is reproduced from those solvents by evaporation unchanged. Its solution in water has an acid reaction; it is not rendered turbid by muriatic acid. It appears to be an acid, as it forms with ammonia a very crystalline mass, from which potash evolves ammonia. Muriatic acid, however, throws down no chloride of selenæthyle from it, which is a proof that oxychloride of selenæthyle was not produced by the action of the ammonia. On the other hand, sulphurous acid separates selenæthyle from the mass.

An elementary analysis, instituted with 0·305 grm. of the substance, gave 13·68 per cent. of carbon and 4·298 per cent. of hydrogen. The determination of the chlorine gave 20·65 per cent. The determination of the selenium was a failure. From these numbers it appears that this substance contains 4 equivs. of carbon to 1 equiv. of chlorine.

Oxychloride of Selenæthyle, $C^4 H^5 SeO + C^4 H^5 SeCl$.—Chloride of selenæthyle is readily soluble in ammonia, forming muriate of ammonia and oxychloride of selenæthyle. If this solution be evaporated, the latter may be separated from the muriate of ammonia by absolute alcohol. It crystallizes in very shining, colourless cubes, which are usually grouped in a stellate form. Muriatic acid precipi-

tates oleiform chloride of selenæthyle from its watery solution, and sulphurous acid produces a stinking mixture of selenæthyle and its chloride. From this behaviour, and what we know of the analogous compound of tellurium, its composition may be inferred with safety.

Bromide of Selenæthyle, $C^4 H^5 SeBr$.—This is deposited in the form of a citron-yellow oil, heavier than water, when hydrobromic acid is added to a solution of nitrate of selenæthyle.

Iodide of Selenæthyle, $C^4 H^5 SeI$.—This is produced when hydriodic acid is added to a solution of the nitrate or chloride. It is a black fluid, of a semi-metallic lustre, heavier than water, and very like bromine. It is inodorous, and does not solidify at 32° F.

These two compounds are readily soluble in ammonia, forming an oxybromide and an oxyiodide. These, however, I have not further investigated.—*Ann. der Chem. und Pharm.*, lxxxvi. p. 35.

On the pretended Occurrence of Iodine in Milk, Eggs, and the Atmospheric Air. By Dr. Lohmeyer.

Some years since, Chatin instituted some investigations upon the distribution of iodine; he not only found it in all spring-waters, in fresh water and land plants, in the most various articles of food, in artificial beverages such as wine and beer, but, according to him, it constantly occurs also as an essential constituent in the inhabitants of our rivers and in land animals.

As it was shown, about the same time, by Meyrac, Marchand and others, that the distribution of iodine is much more considerable than had hitherto been supposed, it could excite no surprise that it should be found in the animal organism; here, as everywhere in nature, it was to be regarded as the constant companion of the chlorine compounds.

Chatin, however, regards iodine not as an accidental, but as an essential constituent of the organs; and according to his statements with respect to the quantities of it contained in eggs, milk, &c., he appears to be perfectly right in so doing. According to Chatin, a hen's egg contains more iodine than 1 litre of milk, whilst this again contains more than our usual articles of food and beverage. He also considers iodine to be of importance in the respiratory process. Normally the air contains 1·500 milligrm. of iodine in 4000 litres, and during respiration 4·5 are said to disappear. Fourcault, who has occupied himself with the study of the causes of goitre and cretinism, examined the air in those places where these diseases are indigenous; in these localities he found the atmosphere free from iodine, and concluded accordingly that the deficiency of iodine was the principal cause of goitre and cretinism. Chatin immediately proved that the air of the Alps was much poorer in iodine than the atmosphere of Paris; he found less iodine in the valley of the Rhone than in that of the Seine, less still in the valley of the Isère, and a constant diminution towards the Alps. He only met with it again in the plain of Piedmont, after it had eluded his investigations on the French side of the Alps.

As therefore the influence of iodine appears to be of the greatest importance to the development and continuance of the animal organism, the author regarded the testing of Chatin's statements as of sufficient importance to undertake it himself with great care.

Goitre does not occur in Göttingen, whilst in some of the neighbouring villages, in Lengden, for instance, it is very frequently met with. If the want of iodine in the air were the cause of the evil, it might be expected that a difference would be presented between the quantity of iodine contained in the air of Göttingen and that of Lengden. The author therefore examined first the air of Göttingen; he allowed 4000 litres of air to pass in small bubbles through a stratum of solution of caustic soda 18 inches in thickness, adding quicklime to the solution from time to time to remove the carbonic acid which was taken up by it. The apparatus was so arranged that the passage of 4000 litres of air required nearly a whole week, so that no iodine could be lost. Nevertheless, on testing for iodine, a negative result was obtained, so that an investigation of the air of Lengden must appear perfectly unnecessary *.

The author has sought for iodine in cow's milk and hen's eggs with a similar result. Thus no trace of iodine was to be found in 12 eggs or in 600 or 6700 grms. of milk. The fluids in which the iodine must be concentrated amounted in all cases only to a few centimetres; for testing them, cold starch-paste and pure nitric acid into which nitrous acid had previously been passed were employed.

The author does not deny, that, by the employment of still larger quantities of milk and eggs, the exhibition of iodine may perhaps be possible, and that under certain circumstances iodine may also occur in the atmosphere, especially in the neighbourhood of manufactories and chemical laboratories; but from his experiments he considers that he may draw the conclusion, that Chatin's statements are to be considered as erroneous throughout, and that the absence of iodine in the air cannot be the cause of goitre and cretinism.—*Nachrichten von der Gesellsch. der Wiss. zu Göttingen*, 1853, p. 131.

On the supposed new Element Thalia.
By Prof. J. Lawrence Smith.

About fourteen months ago the discovery of a new earth was announced by Dr. D. D. Owen as existing in a saponaceous mineral from the amygdaloidal traps of the north shore of Lake Superior. A few months after the first announcement, I obtained 2 or 3 grms. of the mineral from Dr. Owen, and subjected it to analysis without discovering any substance in it that could be called a new element. The results were not made public at the time, as more material was required to arrive at a positive conclusion. It is only lately that, through the kindness of Dr. Genth, of Philadelphia, an additional quantity of the thalite has been obtained, as well as some of the

* The same result was obtained by Mr. S. Macadam of Edinburgh (see Chem. Gaz. for Aug. 2, 1852), with whose researches the author does not appear to be acquainted.—Ed.

earth called thalia. Both have been examined with great care. The analysis of the former accords with my former analysis, making the thalite to be *saponite*. The earth sent as thalia is *magnesia* mixed with a little lime.

It may be well to state here, that the fact of the precipitation of the neutral solution of the earth by oxalate of ammonia seems to have had considerable weight on the original decision concerning this substance. But it is an erroneous impression that oxalate of ammonia will not precipitate the neutral and even slightly acid solution of magnesia salts, more or less promptly according to circumstances, a fact not sufficiently insisted on by writers on analytical chemistry; some experiments on this subject will furnish matter for a future article, in which it will be shown that precautions are frequently required to separate lime from magnesia by oxalate of lime, when the magnesia is present in considerable quantity. Further remarks on this substance will be made when the analysis of thalite is given.—Silliman's *Journal*, July 1853.

On the Recovery of Gold and Silver from the Fluids employed for Electro-plating and Gilding. *By* Prof. Bolley.

The cyanide of gold, dissolved in an excess of cyanide of potassium, resists most means of separation; even sulphuretted hydrogen produces no precipitate in it. The complete separation of the gold cannot be effected in the humid way; and this has given rise to the propositions of Böttcher, Hessenberg, Elsner and others, to evaporate the fluid, mix the dry residue with an equal quantity of litharge, fuse the mixture at a strong red heat, and dissolve the lead from the fused mass by hot dilute nitric acid; by this means the gold is left as a loose sponge. A more recent proposition is that of Wimmer, by which the mass left by evaporating the fluid to dryness on the water-bath is mixed with one and a half times its weight of nitrate of potash, and thrown in small portions into a red-hot Hessian crucible. The explosions must be waited for, and the process continued until the entire mass runs smoothly. The first process has nothing against it, except the necessity of a strong fire and the employment of nitric acid; the second, on the contrary, is very unpleasant and unsafe in its performance. It is sufficiently well known that there is no substance with which nitrate of potash detonates so violently when heated as with cyanide of potassium. If the portions of the mixture employed be only a little too large, very violent explosions are produced, which cannot take place without loss.

The following process may be adopted in small operations with a platinum crucible over a spirit-lamp. The dried mass of salts is mixed with an equal quantity of powdered muriate of ammonia, and gently heated. The ammoniacal salts decompose the cyanides of the metals, forming cyanide of ammonium, which is decomposed and volatilized, whilst the acid of the ammoniacal salt or the halogen combined with the ammonium unites with the metal which had

been combined with the cyanogen. In the present case, muriate of ammonia forms chloride of potassium, chloride of iron (when ferrocyanide of potassium has been employed) and chloride of gold. The latter is readily decomposed, with formation of metallic gold; the other, at least partially, with separation of peroxide of iron, in fine crystalline scales. Undecomposed chloride of iron, as well as chloride of potassium, may be extracted with water after complete decomposition, for which a slight red heat is sufficient; the gold forms a coherent spongy mass; the iron, fine light scales, which are readily separable by mechanical means. If any gold remain in the form of dust with the peroxide of iron, it may be dissolved out with nitromuriatic acid (the calcined oxide of iron long resisting the action of the acid), and the gold thrown down by protosulphate of iron. In most cases this mode of separation will be unnecessary. The author has convinced himself, by the employment of measured volumes of the same solution of gold, evaporation, heating with muriate of ammonia, and so forth, that even the quantity of gold in such solutions may be determined with sufficient exactness.

The same process may be adopted with plating fluids; chloride of silver is obtained together with oxide of iron (from the ferrocyanide of potassium); the chloride is readily dissolved by ammonia; metallic silver, of which however but little or none is formed, is extracted by nitric acid. It is unnecessary to say that the residue is operated upon in the usual manner to obtain the silver; nevertheless, as the decomposition of the plating fluids may be effected in the humid way by means of sulphuretted hydrogen, this process may not be so frequently adopted for silver.

Lastly, it may be useful to inform those persons who occupy themselves with electro-plastic processes, that the employment of chloride of ammonium or a salt of ammonia in this manner, furnishes a ready means of testing the composition of such fluids as are used in the formation of a galvanic coating. For solutions of copper the author employs sulphate of ammonia, because when muriate of ammonia is employed, chloride of copper is formed, which is partially volatilized with the undecomposed sal-ammoniac, producing a loss of copper.—*Polytechn. Centralblatt*, 1853, p. 551.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 16, 1853.

"On the frequent occurrence of Indigo in Human Urine, and on its Chemical and Physiological Relations." By Arthur Hill Hassall, M.D., Physician to the Royal Free Hospital, &c.

The author was led to the investigations laid before the Society in the above communication, by the following circumstances:—

Some three or four years since, when examining urinary deposits under the microscope, he frequently observed in the field of vision particles of a deep blue colour: so often did this occur, that he could not even then help suspecting that their presence was not accidental; however, no analysis of the blue colouring matter was made at that time, and the circumstance was in a fair way of being forgotten, until the recollection of it was revived by another occurrence.

In June 1852, a sample of urine, freely exposed to the air in an open vessel, was observed, after four or five days' exposure, gradually to change colour; the pellicle or scum which had formed upon the surface of the urine became first slate-coloured, and at length deep blue, with here and there a rusty-red tint. The urine also underwent at the same time some remarkable changes; it became thick and turbid, deep brown, greenish, bluish-green, and finally of a faded yellowish-green colour; a considerable sediment was found at the bottom of the glass; this was deep brown, intermixed with a little blue colouring matter, and it had a medicinal smell resembling somewhat that of *Valerian*. In this state, without undergoing any further material changes, the urine remained for many days.

Examined with the microscope, the scum or pellicle on the surface was found to consist of vibriones, innumerable animalcules, and crystals of triple phosphate, with a great many fragments and granules of a deep and bright blue colour.

A second sample of the same urine was therefore procured, taking every precaution to avoid fallacy. Gradually the same changes ensued as in the first sample, and this likewise became blue. Having thus ascertained that the changes observed were due to something contained in the urine itself, the author next proceeded to set aside in open vessels, a series of urines all from the same patient, noting the alterations which occurred from day to day; these samples underwent nearly similar changes; but the quantity of blue colouring matter and brown extractive gradually diminished, until at length they were present in such small amount as to be visible only under the microscope, and at last they entirely disappeared.

The results obtained from an examination of the *urine*, the *blue colouring matter* and the *brown extractive*, are then given by the author; they are as follow:—

The urine.—The urine of the second sample, at the time of analysis, when shaken, had a dark, greenish-brown colour; but on standing at rest for some time, the colouring matter fell to the bottom, forming bluish-green flocculi, while the supernatant liquid was of a deep wine-red colour. The bottle was set aside corked, for ten days, at the end of which time the bluish-green precipitate had entirely disappeared; but on removing the cork, and allowing free access of air for some time, the coloured deposit was again produced. This was washed with water, drenched with hydrochloric acid, and finally dried; by this means was obtained a rich blue powder possessing all the chemical characters and properties of indigo.

The urine that was filtered off from the above precipitate was

allowed to evaporate spontaneously, by which means it yielded an additional quantity of indigo, which adhered in the form of very small flakes to the sides of the dish. It also gave a rather large proportion of a deliquescent brown colouring matter, which was treated, first with alcohol, and then with water.

The alcohol acquired a deep brownish-red colour, and the water a dark brownish-green. Both of these solutions were evaporated at a temperature of 160° Fahr. The alcoholic solution furnished a rich brown extractive which was soluble in water, but not in dilute acids, and nitric acid did not produce that play of colours which is characteristic of bile pigment; nor did the precipitate formed with basic acetate of lead furnish a purple liquid with alcohol and free acid. A strong solution of potash dissolved the extractive and yielded a deep blood-red fluid, which was rendered green and opalescent by boiling. These reactions show that the brown pigment was somewhat like hæmatine in its chemical manifestations.

While the aqueous solution of the brown matter was undergoing evaporation, it gave a further supply of indigo, which was formed most freely at the edge of the liquid. The residue was made black by concentrated sulphuric acid and deep brown by potash.

The blue colouring matter.—Of two samples of this in a dry state, mixed with a large quantity of earthy phosphates, vibriones, mucus, and epithelium, one gave a dark brown solution with concentrated sulphuric acid, and the other a dirty blue. Both of these solutions were decomposed by water, furnishing in the former case a dark brown deposit, and in the latter a dirty green. In most of their other reactions, however, they presented the characters of indigo; and it is especially deserving of notice, that they were reduced by lime and sugar, giving a liquid from which hydrochloric acid threw down a greenish-blue precipitate.

The cause of concentrated sulphuric acid giving with one of these samples a brown solution, and with the other only a dirty blue, was, the author considers, mainly owing to the large quantity of animal matter with which the specimens were contaminated; the acid, from its charring effect on this, would produce a brown or blackish solution, thus obscuring the colour of the solution of indigo.

The brown extractive.—The brown extractive yielded nearly the same results as on its first analysis, and the aqueous solution furnished a few blue flocculi. A portion of the alcoholic extract was heated with Liq. Potassæ for the purpose of ascertaining whether it contained leucine, and the product, on being treated with hydrochloric acid, gave off a powerful odour, which was somewhat like *valerianic acid*; but the result was too doubtful to be of much value. The author had already referred to the peculiar smell of *Valerian* emitted by the extractive of more than one of the samples. He considers that the clearest and most positive evidence was thus obtained that the blue colouring matter in this case was indigo.

It was not very long after the occurrence of the first case of blue urine that numerous other instances fell under the author's observation. The urines of all these cases underwent very nearly the same

changes as in the first; in some, the quantity of blue colouring matter found was very considerable, in others less; and in the third class of cases the microscope was necessary for its discovery. In nearly all these cases the blue colouring matter was submitted to analysis, and ascertained, on the clearest evidence, to be indigo.

The author in the next place considers the question of the source and origin of indigo in the urine.

It appeared that in the cases related by the author, coloured indigo was not present in urine when first voided, but that it was gradually formed some time afterwards by a process of oxidation on exposure to the air, being in most of the cases probably derived from the brown extractive, which in its chemical manifestations so closely resembles hæmatine.

The author contrasts *cyanourine* with the indigo detected in urine. He observes that the most distinctive tests laid down for cyanourine are its solubility in boiling alcohol, and the action of sulphuric acid upon it, which give a reddish-brown solution; and states he had ascertained that these tests are not to be relied upon, since indigo, when contaminated (as in the urine it frequently is) with a large quantity of animal matter, vibriones, &c., gives a reddish-brown solution with concentrated sulphuric acid, from the charring of the animal matter, and in many cases forms a bright blue solution with boiling absolute alcohol; hence he could not help suspecting that cyanourine and indigo are very closely connected with each other, if they be not identical. He observes, it is at least singular, that while so many cases of indigo were met with, not a single instance of cyanourine presented itself. He also contrasts indigo with apoglaucine, and remarks that this is acknowledged by Heller himself to be nothing more than cyanourine mixed with urrhodine.

Taking then into consideration the whole of the facts described in this communication, the following conclusions are deduced:—

1st. That blue indigo is frequently formed in human urine, the quantity being subject to the greatest variation; in some cases it is so considerable as to impart a deep green, or bluish-green colour to the whole urine; a pellicle of nearly pure indigo also extending over the entire surface of the liquid; while in others it is so small that it can only be detected by means of the microscope.

2nd. That for the formation of this indigo, it is in general necessary that the urine should be exposed to the air for some days in an open vessel, oxygen being absorbed and the blue indigo developed. Whatever facilitates therefore oxygenation, as free exposure to light and air, warmth and sunshine, hastens the appearance of the blue indigo; hence in summer the changes described take place much more quickly than in winter; on the contrary, these changes are retarded and even stayed by exclusion of the atmosphere. Blue indigo may even be deprived of its colour and reformed, alternately, according as air is excluded or admitted to urine containing it. From some of the cases recorded, it would appear, however, that blue indigo is occasionally formed in the system, and is voided as such in the *urine.*

3rd. That there is usually found with the blue indigo, where the amount of this is considerable, a brown extractive, sometimes in large quantity, the aqueous solution of which, by exposure to air, yields a further supply of coloured indigo, and which closely resembles hæmatine in its chemical manifestations and elementary composition. There is therefore great reason for believing that in the majority of the cases here recorded, the blue indigo was derived from altered hæmatine, although it is at the same time probable, that in some cases it is formed from modified urine pigment which is itself supposed to be a modification of hæmatine. Between the greater number of the animal colouring matters there is the closest relationship in chemical composition, so that the transformation of the one into the other would appear to be both easy and natural.

4th. That the urines in which the coloured indigo occurs in the largest quantity, are usually of a pale straw colour, readily becoming turbid, alkaline, and of low specific gravity. Small quantities of indigo are however frequently found in urines possessing characters the very reverse, that is, in such as are high-coloured, acid, and of high specific gravity; but, as a rule, in these urines the blue pigment is usually absent.

5th. That as coloured indigo does not occur in healthy urine, and since where the amount of this is at all considerable it is accompanied with strongly-marked symptoms of deranged health, the formation of blue indigo in urine must be regarded as a strictly pathological phænomenon, apparently associated rather with some general morbid condition, than essentially with disease of any one organ; although there is reason for believing that the blue deposit is met with very frequently in Bright's disease, and in affections of the organs of respiration, it should however be remarked that none of the worst cases of indigo in the urine which the author met with were cases of Bright's disease.

The paper is illustrated by drawings, and a specimen of the indigo, as deposited from urine, was exhibited.

PATENT.

Patent granted to William Edward Newton, *for improvements in the Manufacture of Carbonates of Soda.*

In carrying out his improvements, the inventor takes sulphate of soda, as obtained by any of the known processes, and reduces it to a coarse powder; and with this he mixes about one-half its weight, more or less, of powdered coal, charcoal, sawdust, or other combustible matter. This mixture is subjected to a low red heat, in a suitable furnace, until the mass is melted, and thoroughly decomposed into sulphuret of sodium. It is then withdrawn from the furnace, and when cool enough dissolved in water, and run into suitable air-tight vats, provided with pipes and stop-cocks, and con-

nected with each other in the manner known among chemists as Woolf's apparatus; which vats, for greater convenience, are placed one above another. By an air-pump, or other suitable means, carbonic acid is then transmitted through the liquid in the series of vats, entering the lower ones first. It is preferred that this carbonic acid should be obtained from the escape gases from chimneys, or other parts of furnaces burning anthracite or other mineral coal, and especially from the chimneys of steam-boilers. The gases are first passed through water in a suitable vessel, to remove ashes, smoke, or other dirt; a little lime, carbonate of lime, or alkaline matter being mixed with the water in the said vessel, to absorb and remove any sulphurous acid, the presence of which would injure both apparatus and materials. It is found in practice that 1 lb. of lime is sufficient for 10,000 cubic feet of gas.

The carbonic acid is transmitted through the liquid in the vats until the decomposition of sulphuret of sodium into carbonate of soda is found in the lower vat to be complete, which is easily known by suitable chemical tests, when it may be drawn off to be filtered and evaporated in the usual manner. The liquor in the upper vat is then to be brought into the lower one, and fresh liquor into the upper one, and the process repeated as before.

The patentee remarks, that any arrangement of apparatus may be used that will bring carbonic acid into intimate contact with sulphuret of sodium.

During the whole process a constant stream of gases is escaping from a pipe in the upper vat, consisting of sulphuretted hydrogen, nitrogen, and other gases. The whole of the sulphur originally in the sulphate of soda is contained in the sulphuretted hydrogen, which may be recovered, or made into compounds of sulphur by means well known to chemists.

If bicarbonate of soda, or "soda-salaratus" as it is called when impure, is to be made, the solution of carbonate of soda, obtained from the vats wherein the sulphuret of sodium is converted into carbonate by means of carbonic acid, as previously described, is filtered, and boiled down until the carbonate of soda separates from the liquor as a crystalline powder, consisting of 1 equiv. of real carbonate of soda united with 1 equiv. of water; or, if thought desirable, commercial soda-ash or sal-soda may be dissolved in water, and substituted for the solution spoken of above. The powder of carbonate of soda, above mentioned, is ladled out of the liquor, drained, and allowed to cool. This is coarsely powdered and spread upon frames, which are piled one upon another in air-tight chambers. When the chambers are full, the openings are closed, except a vent at the top; and carbonic acid, by preference, obtained and purified, as mentioned in the preparation of soda-ash, is forced into them until the saturation is complete; when the soda will be found to have absorbed a second equivalent of carbonic acid, forming bicarbonate of soda or soda-salaratus, when not pure. The bicarbonate of soda is then taken out, dried and powdered.—Sealed Nov. 8, 1852.

THE CHEMICAL GAZETTE.

No. CCLXIII.—October 1, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Combinations of the Æthylic and Methylic Hydrosulphuric Æthers with certain Metallic Chlorides. By A. Loir.

It is generally admitted that mercaptan is an alcohol, all the oxygen of which has been replaced by sulphur, and that hydrosulphuric æther stands in the same relation to mercaptan as ordinary æther to alcohol. As alcohol and æther combine with certain metallic chlorides to form crystalline compounds, I have endeavoured to produce analogous combinations with mercaptan and the hydrosulphuric æthers. The present memoir treats of the latter compounds.

Æthylic Hydrosulphuric Æther and Bichloride of Mercury, ($C^4 H^5 S, HgCl$).—If to a watery solution of bichloride of mercury we add a few drops of hydrosulphuric æther, or of its alcoholic and ætherial solutions, or even of the water with which it has been washed, numerous fine, interlaced, acicular crystals are deposited on shaking the mixture. When the quantity of æther is too great, a white viscous deposit is formed at the bottom of the vessel. This deposit becomes converted into acicular crystals by contact with a new solution of the bichloride of mercury.

These needles were separated by filtration, washed with cold water and alcohol, and put to dry between paper. Dissolved in boiling alcohol, they furnished on cooling fine, long, delicate, acicular crystals.

Properties.—The compound obtained is colourless, and strongly refracts the light; it diffuses a very disagreeable odour; it is heavier than water. It fuses completely at 194° F. into a colourless, transparent liquid, which on cooling forms crystals which radiate round various centres. Heated in a tube with the flame of a spirit-lamp, it is decomposed, giving a considerable carbonaceous residue, metallic mercury, and thick, white, fœtid fumes. These fumes burn with a green flame, with production of sulphuric and hydrochloric acids. When exposed to the air, the compound loses hydrosulphuric æther and the superficial crystals become opake; its odour is probably owing to an analogous decomposition. By the slow evaporation of solutions in æther and wood-spirit, I have obtained fine crystals belonging to the system of the oblique rhombic prism; the angles formed by the faces are 77° 12′ and 103° 40′; the angle of the base is 73° 10′.

Hydrosulphuric acid decomposes this compound, sulphuret of mercury being formed. If this decomposition be effected by the action of a stream of dry sulphuretted hydrogen gas upon the crystals, abundant fumes of muriatic acid are evolved, and hydrosulphuric æther is condensed. Nitric acid attacks it even in the cold, with evolution of reddish vapours; the liquid resulting from this action contains no sulphuric acid. This is also what takes place with hydrosulphuric æther and nitric acid. Boiling sulphuric acid decomposes it; the liquid acquires a black colour.

Potash and lime render the crystals yellow. Ammonia gives chloroamidide of mercury with an ætherial solution of this substance.

All the elements were separately determined; the methods followed are detailed in the memoir:—

	Found.	Calculated from the formula $C^4 H^5 S, HgCl$
Mercury	55·68	55·36
Chlorine	19·84	19·67
Sulphur	8·43	8·85
Carbon	12·68	13·33
Hydrogen	3·06	2·79

Æthylic Hydrosulphuric Æther and Bichloride of Platinum, $(C^4 H^5 S)^3, PtCl^2$.—This compound is produced under the same circumstances as the preceding. It forms small, orange-yellow, acicular crystals. Its properties and reactions are analogous to those of the preceding. It fuses at 226° F. Heated in a capsule, it burns with a very smoky green flame, and leaves a residue of metallic platinum. The salts of potash are precipitated by its alcoholic solution:—

	Found.	Calculated from the formula $(C^4 H^5 S)^3 PtCl^2$.
Platinum	37·81	37·95
Chlorine	26·43	27·38
Sulphur	12·74	12·33
Carbon	18·84	18·49
Hydrogen	4·58	3·85

By the substitution of methylic for æthylic hydrosulphuric æther in the preceding operations, crystalline compounds are obtained presenting the same appearance, the same properties, and the same reactions as those already described. The mercury and platinum only were determined; the mercury gave 61·09, the platinum 42·74 per cent. The formulæ corresponding with the two formulæ indicated would require 60·24 mercury and 42·64 platinum.—*Comptes Rendus*, June 20, 1853, p. 1095.

Remarks on the Potato Disease. *By* THORNTON J. HERAPATH.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,—During the course of the last few months, that dreadful scourge, the potato blight, has again made its appearance amongst

us, and has already committed great devastation in this and the sister island. My avocations having lately afforded me a few weeks' leisure, I determined to devote it to the re-investigation of the subject, in the hope of ascertaining, if possible, the cause or origin of the disease, as well as a means of curing it or preventing its occurrence. I will not now occupy your time and space with a long account of all the experiments and researches that I have made with this object, but will content myself with making you acquainted with the general conclusions at which I have arrived. They are as follow :—

1. That the potato blight is neither directly nor indirectly caused by the ravages of any parasitical insect.

2. That it is the effect of a species of putrefactive fermentation or incipient decomposition of the nitrogenous, *i. e.* albuminoid constituents of the sap or cell-contents.

3. That this decomposition is either directly produced by a peculiar fungus, the *Botrytis infestans*—to which public attention has been already directed by other writers—or, what is in my opinion a still more probable supposition, the fungus referred to only makes its appearance after the fermentative processes have been in action for some time, and consequently is *an effect*, and not *the cause* of the disease.

4. That the blight has been in some measure produced by the long-continued and indiscriminate use of animal nitrogenous manure, which has over-stimulated the potato plant, and has thus rendered it more susceptible of disease, and has, in fact, produced the same effect upon it that alcoholic drinks, when taken in excess, do on the human system; that is to say, it has injured the stamina of the plant, and rendered the organism more readily affected by atmospheric and other influences.

5. That animal or highly-nitrogenous organic manures should be used with great caution in the cultivation of the potato, and indeed in that of all root crops; the best manure for the potato plant being the inorganic compounds, such, for instance, as those which are, or were at one time, used in some parts of the Continent.

6. That the disease having once established itself, has become epidemic.

7. That it is contagious, if not infectious.

8. That the only mode of eradicating it is to restore the original constitution of the plant.

9. That this desirable result can be only brought about by introducing a complete alteration in the mode of cultivation that is adopted.

10. That the changes in question should consist,—1st, in thoroughly drying the seed potatoes, by the process now followed in some parts of Germany; 2ndly, in steeping them for a short time in a dilute solution of the sulphate of copper (blue vitriol or blue stone), of about the same strength as that used for "pickling" wheat; 3rdly, in planting them in *poor*, *well-drained* land; 4thly, and lastly, in

substituting for the farm-yard manure, &c., now employed, some *inorganic* compost similar to those before alluded to.

In conclusion, I would suggest that the following simple experiment should be tried in storing the potato crop during the present season:—Let the tubers be stored in the usual way, but in the centre of each heap or sackful let there be placed a quantity of *unslaked* lime, not in actual contact with the roots, but enclosed in some porous vessel—an old wicker basket, for instance—and covered over with, and surrounded by, a thick layer of straw or hay. By this means the tubers will be kept *dry*; and as the presence of humidity in the air is a great incentive to putrefactive decomposition, one of the main causes of decay will be removed. The lime, so soon as it has become slaked, may be taken away and employed as manure; and, if practicable, should be replaced with fresh lime. The experiment I have described, it must be remembered, can be easily tried, and would cost but little even if carried out on a large scale; it cannot be productive of any injurious consequences, and will be doubtless attended with beneficial results.

I remain, Sir,

Your obedient Servant,

THORNTON J. HERAPATH.

Mansion House, Old Park, Bristol,
August 17, 1853.

On Arsenious Acid, its Salts, and the Arsenio-sulphurets. *By* O. B. KÜHN.

The author has observed in some arsenious acid which had been separated in concentrically-grouped crystals from a solution of arsenite of silver in nitric acid, the same rare crystalline form which was first observed by Wöhler in the arsenious acid from a cobalt-roasting furnace, and has since been again seen by Pasteur.

The author states that Hirtzell obtained large octahedral crystals by the gradual cooling of a hot solution of ammonia saturated with arsenious acid; when he boiled the fluid for a longer time, making up for the loss of ammonia, he obtained, together with these octahedrons, the other modification, flexible crystals of a pearly lustre, in the form of right rhombic prisms.

If a boiling solution of arsenious acid be added to a solution of neutral nitrate of silver, but little is thrown down; but on the addition of a little ammonia, as much as possible of the yellow powdery arsenite of silver is precipitated. More ammonia does not increase the precipitate; and, moreover, all the arsenite of silver is not thrown down, because it is soluble in the nitrate of ammonia which is produced; consequently no precipitate is produced in fluids which contain a large quantity of this. The precipitate has the composition $3AgO + AsO^3$.

This salt becomes darker and greenish with time. The author also obtained the same salt (not $2AgO + AsO^3$) by mixing together ammonia saturated with arsenious acid and a solution of nitrate of

silver in ammonia (by Filhol's process); nevertheless the precipitate was only produced when he added a considerable quantity more nitrate of silver dissolved in water. Arsenite of silver is readily oxidized by nitric acid. The statements of Pelletier and Laugier as to its stability under the action of nitric acid are not correct. Reynoso's statement, that this salt is soluble in caustic potash, is inaccurate; the salt remains unchanged at first, and then becomes decomposed (like other arsenites of metallic oxides); the solution contains arsenic and arsenious acids, the residue black arseniuret of silver or metallic silver. Arsenite of potash dissolves arsenite of silver.

The addition of a boiling solution of arsenious acid to neutral acetate of lead throws down neutral arsenite of lead; with basic acetate of lead tribasic arsenite of lead is thrown down, and with lime water tribasic arsenite of lime. The substance which is thrown down from the solution of arsenite of potash by means of alcohol probably also contains a tribasic salt, $3KO + AsO^3$.

In a second article, "Upon three Arsenio-sulphurets," the author communicates a series of experiments, from which he draws the conclusion that there are only four arsenio-sulphurets, namely AsS^2, AsS^3, AsS^5, AsS^{10}.—*Archiv der Pharm.*, cxix. p. 267, and cxxi. p. 1.

On a Process for ascertaining the Equivalents of some Fluid Hydrocarbons by means of Bromine. *By* C. Greville Williams*.

In the course of my experiments on the volatile oils, it was found, that, on the addition of excess of turpentine to bromine, in presence of water, the odour and colour of the halogen was destroyed, and a white, aromatic, oily fluid was the result of the action.

Having observed, that, after a certain point, the smallest possible quantity of turpentine was sufficient to determine the formation of the colourless compound, it was conceived that a simple method presented itself for at once ascertaining the equivalents of fluid hydrocarbons.

It was therefore determined to subject the more important oils of the terebric class to an examination by this method, with the intention of ascertaining which of the many multiples of $C^5 H^4$, which have been suggested by various authors, would be indicated.

The experiments of Blanchet and Sell, Dumas, Deville, Soubeiran, and others, on the turpentine hydrates and the artificial camphor, led them to adopt various views with regard to the formula which should be received as the starting-point of the series of which turpentine has been considered the type.

Deville's first experiments led him to the formula $C^{40} H^{32}$, which he subsequently exchanged for $C^{80} H^{64}$, and still later (L'Institut, March 1843, No. 481) for $C^{20} H^{16}$.

In Löwig's work, the results of the various chemists have been translated into the expression $C^{10} H^8$, while others have considered $C^5 H^4$ the more probable formula.

* Communicated by the Author

It is not intended to insist on the correctness of any one of these, but it is submitted that there is strong reason for supposing that the compound previously mentioned consists of single equivalents of bromine and turpentine.

On simply adding bromine or iodine to a non-oxygenated volatile oil, the action is so violent that the products are liable to be ejected, and sometimes the vessel destroyed; but if water be added previous to the addition of the element, the reaction becomes under control.

No hydrogen is evolved under these circumstances, but there is a formation of a hydracid corresponding to the element used.

51 grs. of turpentine were placed in a stoppered bottle with about 20 vols. of water; bromine was then added slowly from a weighed quantity, the vessel being violently shaken after each addition; and when the oily matter which formed began to acquire a pinkish tint, which was not removed by continued agitation, the vessel containing the bromine was re-weighed, and it was found that the 51 grs. of turpentine had required 117 grs. of bromine for saturation.

It is hardly necessary to remind the operator that the experiment may be reversed, and a given quantity of bromine be placed in a stoppered flask, and the turpentine be added from a weighed quantity, contained in a Schuster's alkalimeter, which is by far the more convenient method, as, from the bromine sinking to the bottom and the turpentine floating on the top, no combination takes place until the stopper has been replaced and the vessel shaken; therefore we avoid the succession of explosions which in the first way of operating occur, from the bromine being dropped through a layer of turpentine.

If we now submit the numbers obtained as above to calculation, we shall find that—

I. 117 : 51 : 80 : 34·8.

In another experiment, made some weeks afterwards, and by the second method, 60·8 bromine required 26·5 of turpentine to form a colourless compound, and—

II. 60·8 : 26·5 : 80 : 34·8,

being exactly the same result.

Bromine being taken at 80, and $C^5 H^4 = 34$.

The next point was to ascertain the values that would be obtained by subjecting oil of lemons and some others of this class to the same process.

In the case of the latter oil, the reaction was far more violent, and a considerably greater amount of heat was developed:—

III.	65·6 grs. bromine required	28·9	turpentine.
IV.	30·65	13·45	lemon-oil rectified below 353°.
V.	51·00	21·00	lemon-oil not rectified.
VI.	60·80	24·50	lemon-oil not rectified.
VII.	34·10	14·85	juniper-oil rectified at 340°.
VIII.	44·50	20·20	juniper-oil not rectified.
IX.	32·55	15·40	savin-oil rectified at 400°.
X.	51·50	27·70	savin-oil not rectified.
XI.	36·80	16·90	lavender-oil rectified at 365°.
XII.	30·50	12·3	caoutchoucine (caoutchine).

On reducing these numbers to per-centages, we have the following values:—

	Theory.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Br...	1=80	70·8	70·3	70·3	70·1	70·2	71·45	72·14	70·3	69·5	68·6	65·71	69·2	71·94
C^5H^31	33	29·2	29·7	29·7	29·9	29·8	28·55	27·86	29·7	30·5	31·4	34·29	30·8	28·06

A highly rectified fluid hydrocarbon (boiling tolerably steadily at 300°), produced by distillation of bituminous shale, gave on combustion with chromate of lead—

		Mean of two experiments.
Carbon.....	85·7	84·00
Hydrogen ..	14·2	14·17

XIII. 62·95 of this liquid formed a colourless compound with 40·2 of bromine, or—

Carbon.....	51·32	18	52·4
Hydrogen.....	8·65	18	8·7
Bromine	38·90	1	38·9

Oil of lavender, which has been represented by $C^{15}H^{12}$, will be seen to come within the same formula as turpentine.

It has been found by numerous experiments, as might have been foreseen, that volatile oils which have become oxidized by exposure to the air, require less bromine to form a colourless compound.

The above synthetical results have been calculated on the supposition that 1 equiv. of hydrogen is expelled from the oil in the act of combination, for it is generally supposed, that by the action of the halogens on these oils, one-fourth of the hydrogen is removed, and that the element supplies its place according to the laws of substitution, while the hydrogen displaced is imagined to form a hydracid with the excess of the haloid; but I have constantly found in the experiments quoted, that although the liquid floating above the oily bromides has in all cases an acid reaction, that the amount is small and variable; in the experiments I. and II., 11·6 and 13·4 grs. of carbonate of soda were required to saturate the acid formed.

As no hydrogen is evolved by the action of bromine, the equation $C^5H^4+2Br=C^5\left\{\begin{matrix}H^3\\Br\end{matrix}\right.HBr$ is required to satisfy the conditions; but we have seen that only 1 equiv. of bromine is necessary to the reaction; it would therefore appear to be indicated, that the element, under the circumstances mentioned, combines with turpentine without decomposition, or formation of C^5H^3; nevertheless, it was not considered justifiable to calculate the results obtained in accordance with this idea, as these questions can only be solved by a rigorous examination of the products of decomposition of the oily bromides, for it is by no means easy to obtain analytical results of such accuracy, as to show correctly a difference of 1 equiv. of hydrogen. The decomposition of the bromide of turpentine by zinc in sealed tubes has afforded results, which, it is confidently hoped, will lead to the elucidation of this part of the subject.

It is submitted that the numbers in the table indicate a close approximation to C^5H^3Br; and in several experiments with other

oils, numbers were obtained, sufficiently near to the theoretical values, to show most clearly that either $C^5 H^5$ or $C^5 H^4$, and not a multiple of that formula, is the true constitution of the molecule of the oils of this series, which combines with 1 atom of bromine.

Laboratory, Oxford Court,
Sept. 22nd, 1853.

ANALYTICAL CHEMISTRY.

On the Analysis of Cast Iron.

By Professors CAMPBELL MORFIT *and* JAMES C. BOOTH*.

[Extract from the Official Report to Captain L. A. B. Walbach, U.S. Ordnance, on Foundry Service, upon the Examination of Gun Metal.]

THE associated substances always occurring with the ores in the furnace, are silica, lime and alumina; in addition to which, sulphur, phosphoric acid, oxide of manganese, magnesia, and the alkalies are rarely absent. Substances of more unusual occurrence are oxides of chromium, tin, titanium, vanadium, copper, arsenic, and some others. Now, although most of these substances are reduced to their metallic state with great difficulty by the fuel and high heat of the furnace, yet their affinity for oxygen is weakened, and the contact of a large quantity of metallic iron adds its influence to reduce portions of them to metal, in which state they enter into combination or admixture with the iron. Hence crude cast iron or pig iron, besides its essential constituent carbon, contains more or less of the elements of the ingredients above named, though always in small proportion to the iron, and in their total amount rarely exceeding 8 to 10 per cent.

The influence of these associates upon the character of cast iron has been determined to a limited extent, and in the case of only a few of them. Thus a considerable proportion of manganese is said to impart a large lamellar and brilliant fracture and some degree of brittleness; phosphorus is supposed to render iron "*cold short*," and sulphur "*hot short*." But the full extent of influence of these few is yet undecided, while the influence of most others is either unknown or at least subject to great doubt.

Although most of the above are only occasional constituents, and exist, when present, only in minute quantities, still it was expedient that the examination should be made with a view to the detection of each and every one of them.

Pulverization.—It was found, after repeated trials, that the only sure way of obtaining samples of uniform composition was to clip off pieces of the size of one-eighth to one-tenth of an inch diameter, by means of a cold chisel and hammer. These were taken from the small broken cylinders, which had been bored from the muzzle of the gun, and had served for the mechanical tests. Reduction under

* Communicated by the Authors.

the pestle and sifting should be avoided, for any process which requires that the metal shall be acted upon in a state of *powder* is defective; because the slag and graphitic carbon being as it were mere mechanical components pervading the mass of iron, and not chemically combined with it, form finer particles by pulverization, which from their low specific gravity fly off partly as dust. This loss, and the difficulty of reducing the metallic granules to the same state of fineness as the siliciuretted and carburetted constituents of the metal, prevent the possibility of obtaining a mixture sufficiently uniform to afford a fair average sample. We found that equal portions of the same powder gave under the same circumstances variable results, whatever solvent was employed. Thus 1 grm. digested in nitromuriatic acid gave of insoluble residue, in two sets of experiments similarly conducted,—

Total Insoluble Residue.

Sample	I.	II.
a.	0·0456	0·0486
b.	0·0480	0·0682
c.	0·0436	0·0568
d.	0·0460	0·0612

These were selected indiscriminately from more than twenty experiments, all of which yielded results that are equally conclusive. In several trials the proportion of insoluble residue obtained from the samples of *dusty* metal presented a greater variation than those from the clippings or even the fine granules. The discrepancy arises from the facts just mentioned. It is also because the mixed metal, in its finest state of comminution, is peculiarly sensitive to a decomposing or transforming action of the digesting liquids, which, instead of being confined solely to effecting solution of the metallic bases, extends to the transmutation of some of the other constituents into soluble matter, as will be treated of in the paragraphs relating to the estimation of carbon, "slag" and silicium. It is therefore imperative that, first, in reducing the metal mechanically, it must be to clippings, and not to powder. The size should be from one-eighth to one-tenth of an inch diameter, as this bulk is better adapted to ensure a gradual reaction and uniformly exact results.

Total Amount of Carbon.—The important bearing of this ingredient upon the quality of cast iron renders its accurate estimation of paramount importance; for the metal is classified into *gray* and *white* varieties, according to the condition in which the carbon exists in it. For instance, in gray iron there is both combined and free (graphitic) carbon, while in the white the carbon is wholly or nearly all combined with the metal. Now as the only way of accurately determining the former condition is by deducting the graphitic from the totality of carbon, it is essentially important that these last two should be estimated with great precision. The most usual method of determining the whole of the carbon is to ignite 5 grms. of the finely powdered metal in a combustion-tube with a mixture of anhydrous chromate of lead and chlorate of potash, or

with oxide of copper. By the aid of high heat and the oxygen generated by the decomposition of those highly oxidizing bodies, the carbon burns off as carbonic acid, and is condensed by caustic potash contained in a bulbed receiver. The increase of weight which the latter acquires by the process of combustion represents the amount of carbonic acid absorbed, whence the total amount of carbon is calculated. This plan, although expeditious, is liable to many objections, the chief of which is the necessity of having the metal in an impalpable powder in order to effect its complete combustion. This entails the disadvantages enumerated in the paragraph upon *pulverization*. It will also be necessary, in most cases, to repeat the ignition in order to check doubtful results.

Another and very accurate method is that proposed by Berzelius, which consists in depositing a weighed lump of 5 grms. of metal upon a fused cake of 30 to 40 grms. of chloride of silver in a vessel containing water, and closely covered to prevent access of air. A little hydrochloric acid is added to promote the action. The silver salt, gradually decomposing, gives up its chlorine to the *bases* of the metallic iron, which by the union become soluble in the water as chlorides, while the eliminated carbon, silicium, and slag subside to the bottom upon the silver cake, which is more or less reduced to the metallic state. The liquor being filtered off through a small paper, the undecomposed portion of chloride of silver is removed with a platinum-pointed pincette, freed of adhering particles by means of the wash-bottle, and reserved for use at another time. The contents of the filter, while still moist, are to be rinsed out into a beaker, treated with dilute nitric acid, and gently warmed to dissolve the reduced silver powder and any traces of oxide of iron. Great care must be observed to provide against too much heat, so as to prevent portions of the carbon from being converted into soluble artificial tannin. When the whole of the silver and oxide of iron have been taken up, the liquor is filtered on a balanced filter, which is washed with hot water, dried first in a hot-air chamber, and finally *in vacuo*, and weighed. The gross amount of carbon, silica, and slag is thus obtained. By ignition, the whole of the carbon is burned off, and the amount determined by weighing the calx. The difference between the two weights, which is the amount lost by the ignition, represents the carbon.

Solution of chloride of copper has been suggested as a substitute for the solid chloride of silver, and its action is more energetic and rapid; but the objection to the plan is, that a small portion of the carbon is lost as carbohydrogen gas.

The above plan has the advantage of giving the total carbon in one operation; but it is tedious, time-consuming, and only manageable with difficulty. Ten to twenty days are necessary for the perfect completion of the operation; and if any air should accidentally enter the digesting vessel, the consequent formation of hydrated peroxide of iron is a serious impediment to the progress of the reaction. The traces of hydrochloric acid, with which the water may be acidulated, tend to prevent the generation of this oxide; but it

must be used sparingly, since otherwise by taking up some of the metallic iron a part of the carbon might be driven off. Free chlorine has also been proposed by Berzelius; but its use is less practicable than the preceding method, because bulbed glass apparatus, requiring nice arrangement and careful management, must be employed by his mode. There is, moreover, difficulty in volatilizing all the chloride of iron formed, and also in preventing the access of air, which by its oxygen will convert some of the carbon into carbonic acid or oxide, or both.

Another process by the same distinguished chemist consists in subjecting the iron in filings to the spontaneous action of dilute but perfectly pure nitric acid, added portion-wise. It is time-consuming, and requires great attention to ensure uniform reaction; for much heat is eliminated, and may raise the temperature of the mixture above 125° F., and thus promote the transformation of a portion of the carbon into soluble matter, as mentioned in the paragraph relating to graphitic carbon. Moreover, a basic salt of iron, soluble with difficulty in cold acid, is likely to be formed. Besides, if any of the foreign alloys are convertible into insoluble oxides by the nitric acid, they remain with the carbon and silicium; and in the after-separation of the former from the latter by ignition, they may, by entire or partial volatilization with the carbon, lead to error in its estimation.

Berthier's process of estimating the total amount of carbon, in slowly oxidizing the iron by exposing it to air and moisture, is tedious, and tends to error, from the fact, that the hydrochloric acid required in the after part of the operation, to dissolve out oxide of iron, as well as the subsequent evaporation to dryness to render the silica, &c. insoluble, subjects the carbon to a partial conversion into soluble humus.

After repeated trials, and due consideration of the above and other processes for estimating the total amount of carbon, we were convinced that none of them possessed that union of speed and accuracy which is necessary to a satisfactory performance of the analysis. We therefore abandoned them, and proceeded to a course of experiment, with the view of elaborating a process which would be rapid as well as reliable; and succeeded in developing the following method:—

1 grm. of metal clippings, accurately weighed, is placed in a small beaker with the atomic proportion of iodine, say 5 grms. of iodine to 1 of metal; a little water is added, and the glass with its cover on left at rest in the cold. Five to six hours suffice for completing the solution of the bases; and the rapidity of action is inversely as the state of dilution of the liquid, so that only enough of water to cover the mixture should be employed. Perfect solution is recognised in the dark brown liquid by the flocculent character of the insoluble matter, as compared with the heavier and metallic particles; and if any of the latter still remain unacted upon, they will subside heavily to the bottom. In such case a few more grains of iodine must be added, if the first portion has entirely dissolved, and

the digestion arrested by filtration, as soon as the solution of the metal has been accomplished, for a prolonged action of the iodine, as well as too great dilution, promote the oxidation and volatilization of the carbon.

Great care must be observed to temper the reaction, which, when too violent, gives off a distinct odour analogous to that of chloride of sulphur. *Slight* additions of water therefore become occasionally necessary, for undue warmth is apt to induce the conversion of a portion of the carbon into soluble matter. This reaction is particularly evident when the metal is in very fine powder. Water is probably decomposed, the oxygen going to the carbon and iron, and the hydrogen to the iodine, which then, in its compounded hydriodic acid form, unites with the oxide of iron.

For example, we present a few results, selected indiscriminately from many equally conclusive, which not only show the difference between the digestions with iodine at hot and cold temperatures, but also the inequality of the "hot carbon," results owing to the difficulty of so regulating the heat as to produce uniformity of reaction:—

	Clippings digested with iodine in the cold.	Powdered metal digested with iodine on the sand-bath.	
	Total carbon.	Total carbon.	
No.	I.	I.	II.
m.	0·046	0·037	
n.	0·039	0·024	
k.	0·038	0·028	
p.	0·045	0·022	
e.	0·042	0·0085	0·024
f.	0·044	0·034	
g.	0·026	0·016	
h.	0·033	0·029	0·0285
j.	0·039	0·0255	0·0380
c.	0·034	0·016	0·0255

When it is evident that no fine particles of metal remain at the bottom of the beaker, the solution is perfect; and the insoluble matters, consisting of all of the carbon, slag, some silica, and a portion of oxide of iron, formed as mentioned under "slag and silicium," float in the liquid, which contains the bases or remaining constituents as iodides. The solution is to be immediately diluted with water, filtered through a balanced filter, washed with hot water, then with hydrochloric acid to remove traces of sesquioxide of iron, and finally with hot water. The filter is then first dried between folds of bibulous paper, and subsequently *in vacuo*, along with the counterpoised paper. The two are then weighed against each other, and the difference of weight denotes the amount of insoluble residue. As this latter does not consist wholly of carbon, but also contains slag and some silex, and perhaps alumina, the filter must be transferred to a platinum crucible, cautiously ignited over a lamp, and finally by the blast, until every particle of carbon is burned off, as may be known when the residual calx presents no

black specks, and again weighed. The loss by ignition represents the total amount of carbon contained in the iron, and is to be determined by deducting the weight of the calx from the weight of the calx and carbon combined.

The filtrate is rejected because of the large excess of iodine which it contains, as the evaporation to dryness with hydrochloric acid requisite for its expulsion would so diminish the phosphoric acid as to render its estimation from such a solution inaccurate.

Allotropic or Graphitic Carbon.—We have already stated that the carbon in cast iron may exist in two conditions, combined and free; in the latter, or free state, it is usually termed graphitic carbon, from its identity with native graphite or plumbago, possessing the same chemical composition, viz. being essentially pure carbon, and the same external character of scaly structure, colour, greasy feel and softness. Regarding the diamond as one form of pure carbon and graphite as another, they have been termed allotropic conditions of that element; and hence, in speaking of the graphitic variety, we have termed it allotropic.

White cast iron contains all the carbon in a state of combination if it be rapidly cooled after fusion; but by slower cooling, a portion of the carbon is eliminated or precipitated through the mass in the form of graphite, the black scales of which contrasting with the whiter colour of the metal, give the appearance of *gray* iron. Where the precipitation takes place only in spots, the metal is termed *mottled.* This artificial graphite is equally resistent of chemical agents as the native plumbago; and since the combined carbon, when separated from cast iron by chemical agency, is easily acted upon, we availed ourselves of their different behaviour to determine their relative quantities. In our first essays we followed the method of Karsten for estimating the allotropic carbon, because it had the sanction of high authority; but we found by experience that it is unsatisfactory. The process consists in dissolving a given weight of the powdered metal in nitric acid by gentle heat, adding a little hydrochloric acid towards the end of the digestion, to ensure the solution of any undecomposed silicide, oxide, or phosphide not wholly soluble in single acids, and to prevent the formation of insoluble sub-nitrates, which are apt to be generated when nitric acid alone is used. After perfect solution, the whole is passed through a balanced filter, washed with hot caustic potash solution to remove extractive matter, then with hot water and hydrochloric acid, and again with hot water. The filter, after being dried between paper and *in vacuo* with its counterpoise, is weighed against the latter. The difference between the two expresses, quantitatively, the contents of the filter, which consist of carbon, slag, and some little perhaps of silica. They are separated by transferring the filter to a platinum crucible, igniting and re-weighing. The calx remains, but the carbon is burned off, and the loss in weight indicates its amount.

It is so very difficult to regulate the action of the nitric acid, that inequality of results is unavoidable. For example, carbon is varia-

bly sensitive to the action of nitric acid, according to its strength and the temperature. At the moment of elimination it is in an impalpable state, which is peculiarly conducive to chemical action. Nor is this behaviour confined solely to the combined carbon, for under the unavoidable circumstances of the digestion, the allotropic carbon is likewise altered, as is proved by the few following examples, selected from a series. Allotropic carbon is particularly changed by the *prolonged* digestion which is necessary to effect perfect solution; and if *fuming* nitric acid is added to facilitate the reaction, the complexity of the change is augmented, and an irremediable source of error created. The annexed results not only lack uniformity in the two series, but also show in the first a much less proportion of allotropic carbon than really exists in the iron, as is confirmed by the results of a correct process, given on the succeeding page:—

	Allotropic carbon.	
No.	First essay.	Second essay.
a.	0·0106	0·0295
b.	0·0150	0·0350
c.	0·0156	0·0350
d.	0·0160	0·0314
e.	0·0210	0·0085

Even slight differences in temperature and strength of acid induce important changes; and when the latter is very concentrated, an electrical phænomenon ensues, whereby the iron is changed into the passive state, and thus rendered insoluble. After some thirty experiments, with results like the preceding, we abandoned Karsten's process as erroneous in principle and fact, and consequently discarded the results obtained by it. The essays to which this disappointment led were more propitious, and ended in a modification of Bromeis's process, which fulfils every requirement.

The allotropic carbon is to be estimated by digesting 1 grm. of clippings of metal at a gentle heat with hydrochloric acid of spec. grav. 1·1. In a few hours the soluble ingredients of the metal will have dissolved, leaving the carbon in flakes or lumps, along with some silica floating or suspended in the liquor. The sediment is to be collected upon a counterpoised filter, washed with hot solution of potash of spec. grav. 1·29 to remove humus and extractive, then with dilute hydrochloric acid, and finally with hot water. The last washing must be perfect, because if any alkaline chloride is retained, being volatile, it will mostly pass off with the carbon during ignition, and thus cause error in the determination of the latter. The filter is then dried, first between folds of paper, and subsequently *in vacuo*, with its counterpoise; and the two are afterwards weighed against each other, and the difference in weight noted. It will be observed, on examination, that the carbon is in scales, and remarkably free from dusty particles. The filter and contents are now to be transferred to a platinum crucible, ignited cautiously over a "Russia lamp," and weighed. The loss by ignition expresses the amount of allotropic carbon contained in the samples, and may be

ascertained by weighing the calx, and deducting its weight from the original weight of the filter and contents.

There are certain requisite precautions to secure the accuracy of this process. Great care must be observed, in the ignition, to burn off all the graphite, so that not even a black speck may be visible in the calx. All draft must likewise be prevented, for particles of the calx may be accidentally blown off, and error thus occasioned, since the loss would be estimated as loss by ignition, and the amount of graphite thus erroneously augmented.

In the reaction with the acid, it is designed to restrict the agency of the hydrochloric acid, as to the carbons, solely to the conversion of that which is in a combined condition into gaseous carbohydrogens and humus, which is easily soluble in a solution of caustic potash. We have, however, found that it is necessary to limit its strength, in order to effect this change without simultaneously altering the allotropic carbon. For example, if the density of the acid is too great and the temperature too high, the results will be variable and unsatisfactory, as is proved by the following experiments:—

	Allotropic carbon.	
No.	I. Strong acid.	II. Weaker acid.
m.	0·0159	0·0170
o.	0·0110	0·0042
q.	0·0152	0·0095
r.	0·0181	0·0138
s.	0·0055	0·0130

It is evident, therefore, that strong acid and a high temperature not only cause the entire transformation of the combined, but induce a partial alteration of the allotropic carbon; so that the results will be constantly varying according to the varying circumstances and to the prolongation of the digestion. On the other hand, the acid must not be too dilute, nor the temperature too low, else the converse of the above will happen; and owing to deficient action, a portion of the combined carbon, instead of having passed off in gaseous and soluble forms, will remain in fine powder with the allotropic carbon, to contaminate it and hinder its correct estimation. A little experience and care will ensure a well-conducted manipulation, and consequently correct results.

Combined Carbon.—The combined carbon is determined after the estimation of the *total carbon* and the *allotropic carbon* separately, by deducting the weight of the latter from that of the former; the difference expresses the amount of the combined carbon. As this method by subtraction is the only available one, it is therefore imperative to have correct figures in order to obtain accurate results.

Silicium and Slag.—Having believed that the silicium and slag, either conjointly or separately, were important constituents as influencing the quality of cast iron, our experiments for separating and estimating them accurately were numerous and varied. The silicium is a chemical component of the iron, while the slag is a

mechanical ingredient pervading its mass like the allotropic carbon. This slag also contains silicium, but as silica, and in combination with earthy bases and oxide of iron; hence in separating the silicium of the metal, it is necessary to avoid decomposing the slag at the same time, and thus taking up also a portion of its silica or bases.

The silicium exists originally in combination with the metal as silicide of iron, and becomes oxidized into silica during digestion with acid, &c. The slag is an accidental ingredient. It is therefore important to determine quantitatively these two conditions; a task not without difficulty, owing to a certain similarity in the behaviour of silex and of slag, respectively, to the reagents necessarily employed as solvents.

It is necessary to digest a new portion of clippings for the estimation of these components. The filtrate from the digestion with iodine for *total carbon*, as well as from that with hydrochloric acid for *allotropic carbon*, will not answer, for the following reasons:—

In the iodine digestion at cold temperatures all the iron is taken up, but a portion of the alumina as phosphate and probably the lime and magnesia are left with the untouched carbons, silica and slag, so that these would not be correctly represented by the weight of the insoluble residue. In numerous essays, repeated for verification, the quantity of the so-called slag and silex was invariably larger than that obtained with nitric or hydrochloric acid. Moreover, as it is difficult to prevent access of air, a small quantity of a basic salt is formed, which is not entirely removed by the hydrochloric acid used in the final digestion, but tends to unite with the silica during ignition, and form a silicate resembling slag, whereby the normal slag is contaminated. The aluminium, calcium, magnesium and phosphorus are oxidized by the oxygen of the water in the presence of the iodine. The large amount of slag always obtained by the digestion with iodine induced at first the belief that the oxide of iron associated with it was free, and had originally existed as such in the metal, and being an oxy-base, was not touched by the iodine, nor yet by the hydriodic acid formed, owing to a deficient quantity of the latter. This view was founded on the fact, that digestion in acids, especially the hydrochloric, which leaves no basic salt, always gave less slag.

Nor can the slag and silicium be estimated from the hydrochloric digestion for *allotropic* carbon, because the solution would in that case have to be evaporated to dryness before filtration, in order to render all the silica insoluble; a process, which, by concentrating the acid and augmenting the temperature, might endanger the partial conversion of the carbon into soluble humus and extractive; besides, the strength of the acid for the gaseous transformation of the carbon would have to be necessarily so high, that it might decompose the slag. The only course is to take a new portion, and to treat it as follows:—

1 grm. of clippings of metal having been accurately weighed, is to be placed in a wide-mouthed flask. A funnel and a drying tube filled with fused chloride of calcium are adapted to the flask by

means of a tightly-fitting cork, and an exit tube, drawn out to a fine opening at its extremity, is fitted in like manner to the further end of the drying tube. Having made certain, by actual examination, of the tightness of the joints, chemically pure hydrochloric acid, of spec. grav. 1·06, is then poured into the flask through the funnel-tube, and the flask slightly warmed to start the action; gases are soon generated, and after having passed over a sufficiently long time to expel all atmospheric air from the interior of the flask, a lighted taper is applied to the fine orifice of the exit-tube, so as to ignite the issuing jet of arseniuretted or mixed gas which is formed from the elements of the contents of the flask. The burning jet is projected against a piece of cold white porcelain. If after five minutes of uninterrupted combustion there is no adhesive tache formed upon the porcelain, it is evident that there is no arsenic, since this process detects less than 1-50,000dth part of a grain of that metal with certainty.

Great care must be observed with regard to the character of the tache, for phosphuretted and antimoniuretted hydrogen gases both give dark stains in a similar reaction; if it is not adhesive, no attention need be given to it, as it is merely a distillate of oily hydrocarbons or phosphorus sublimate. Moreover, if it is a long time in being generated, it may be estimated as a trace; but if it is large and distinct, and prompt in appearing, then it must be quantitatively determined from the same sample as the sulphur, as hereinafter directed. This precaution about the tache is particularly necessary also for the reason that the odour of the phosphuretted hydrogen, as eliminated when iron is dissolved in hydrochloric acid, so nearly resembles that of the corresponding arsenic gas as to be mistaken frequently for it. In the reaction the water is decomposed; its oxygen goes to the iron, which then unites with the acid; while its hydrogen in the nascent state joins with the eliminated arsenic, antimony and phosphorus, and passes over in a gaseous inflammable state. The qualitative test for arsenic, at this stage of the process, is a convenient saving of the time and trouble of a separate digestion, and is no hindrance; for when the test is completed, the apparatus is to be taken apart, and the flask, covered with a watch-glass, transferred to the ledge of the sand-bath, and there left until the residue becomes flotant. Solution is then complete, and the liquid must be evaporated to dryness, re-digested in very dilute hydrochloric acid, filtered, washed with hot water and hydrochloric acid, and lastly with hot water. After drying the filter, it is ignited in a platinum crucible over a "Russia" lamp to burn off carbon, and then weighed to ascertain the amount of residual calx, which consists of silex and slag.

Care must be observed not to use acid stronger than spec. grav. 1·06, or the slag will be attacked and its bases dissolved; nor must it be weaker, as it will cause loss of time in the digestion.

The insoluble portion on the filter must be invariably washed with hydrochloric acid, to remove any traces of iron or oxide that may remain accidentally, and which would afterwards add undue weight to the slag, for it is not removable by subsequent boiling with potash solution.

Having obtained the silica and slag together, and accurately noted their united weight, they are transferred from the platinum crucible to a small silver capsule, and boiled for two minutes with a half fluid ounce of caustic potash solution of 1·10 (spec. grav. 1·25 diluted with 2 vols. of water). After sufficient repose for the subsidence of all suspended particles, which from their extreme fineness would otherwise pass through the paper, it is filtered on the finest paper, and washed with hot water until the filtrate leaves no stain when heated to dryness on a platinum spatula. Silica is dissolved, and the slag remains untouched.

Ley of greater density than above prescribed would decompose the slag by abstracting its silica, while a lesser strength would not take up all the free silica. Nor is carbonate of soda, even in dense solution, a good substitute; for although it may imperfectly dissolve silica while boiling, it cannot retain it on cooling, but deposits it partly in a free state and partly as soluble silicate of soda. The strength before directed has been found by experiment to answer best; it takes up the silica while hot, and retains it on cooling, but does not attack the slag.

After the filter has been washed and dried, it is ignited in a platinum crucible and weighed; the weight expresses the amount of slag, and this, deducted from that of the silica and slag united, gives the proportion of soluble silica, whence its content of silicium is to be calculated.

[To be continued.]

Volumetrical Determination of Sulphuric and Hydrochloric Acids. *By* M. Levol.

The following method has been employed for some time by the author for rapidly determining the per-centage of these acids in commercial substances.

Determination of Chlorine.—The excellent process introduced by Gay-Lussac loses the advantage of rapidity in obtaining results when the per-centage of the element to be determined is not known approximatively; again, when there is an excess of chloride present, it is very difficult to render the liquid clear by shaking, and filtering occupies too much time.

These practical difficulties induced the author to take advantage of the fact, that the phosphate of silver, as well as all silver salts that are more soluble than the chloride, are decomposed by the alkaline chlorides. Thus when a solution of chloride of potassium or sodium is poured upon a precipitate of carbonate or phosphate of silver, there are formed on the one hand chloride of silver, and on the other carbonate or phosphate of the alkali. Consequently when nitrate of silver is poured into a liquid containing alkaline chloride and phosphate, there cannot be any precipitation of phosphate of silver until the whole of the chlorine has been removed from solution. On adding nitrate of silver to a solution of alkaline chloride mixed with ordinary phosphate of soda, the precipitation of the yellow phosphate of silver indicates the point at which the whole of the alkaline chloride is decomposed.

The following is the mode of operating:—About 1 grm. of the salt whose per-centage of chloride is to be determined is dissolved in about 50 cub. centims. of distilled water, and mixed with one-tenth the volume of a cold saturated solution of ordinary phosphate of soda, which must of course be perfectly free from chlorine; if the solution is acid, it must be neutralized with pure carbonate of soda. A solution of nitrate of silver, of known metrical value, is then added from a burette indicating tenths of a cubic centimetre until the precipitate formed *retains* a faint yellow tinge. The first drop of the nitrate produces a yellow precipitate, because it is for the moment in excess at that part of the liquid; but this colour disappears rapidly and entirely on shaking whenever there is a trace of alkaline chloride left.

Determination of Sulphates.—The author effects this by means of nitrate of lead of known metrical value; when the liquid to be examined contains a free acid, it is neutralized by carbonate of magnesia. A 10 per cent. solution of iodide of potassium is then added in quantity just enough to communicate to the precipitate formed, on adding the first few drops of nitrate of lead from the burette, a yellow colour, which disappears on shaking. The end of the operation is indicated in this case, as in the chlorine determination, by the permanent yellow tinge of the precipitate after shaking. The manipulation is the same in both determinations, and is likewise very simple.

The liquid employed for the determination of chlorine contains in 1 cub. centim. 0·03054 grm. of silver, equivalent to 0·010 of chlorine, = 1 grm. in 100 cub. centims.

The liquid employed for the determination of sulphuric acid contains 0·04138 grm. of nitrate of lead in 1 cub. centim., equivalent to 0·010 grm. of anhydrous sulphuric acid, =1 grm. in 100 cub. centims.

With these liquids the results obtained have a per-centage expression; they are accurate to within 0·50 or 0·25 per cent., and occupy only a few minutes. It is obvious, that before applying these methods, it must be ascertained whether the salts to be examined contain any substance besides sulphuric acid and chlorine, which might be precipitated by the test-solution.—*Bulletin de la Soc. d'Encouragement*, April 1853.

Note on the Separation of some Metallic Oxides.

By M. Flajolot.

It is impossible to separate copper exactly from zinc and nickel by means of sulphuretted hydrogen, the sulphuret of copper always carrying down a noticeable quantity of the sulphurets of the other metals even in acid liquids.

The two following methods, on the contrary, allow us to isolate this metal:—

First Method.—A solution of hyposulphite of soda is added to the boiling metallic solution, which is acidulated with sulphuric

acid; sulphuret of copper is formed, which is treated in the usual manner. By this process the precipitation of the metals of the three first classes is avoided.

Second Method.—An excess of sulphurous acid is added to the metallic solution; hydriodic acid is then added; iodide of copper is formed, which may either be weighed directly or converted into oxide. In this manner the copper is separated from manganese, iron, zinc, nickel, cobalt, arsenic and antimony.

Separation of Copper and Mercury.—The liquid is neutralized with carbonate of soda, and an excess of cyanide of potassium is then added. Hydrosulphate of ammonia only precipitates the mercury from this solution.

Separation of Manganese and Cobalt from Nickel and Zinc.—The excess of acid in the solution is neutralized by means of carbonate of soda; an excess of cyanide of potassium is then added, and afterwards carbonate of soda. At the temperature of ebullition the carbonate of manganese is precipitated alone.

It is sufficient then to destroy the cyanide by an excess of acid, to enable the cobalt to be precipitated by carbonate of soda.

When copper is determined by means of hydriodic acid, bismuth is found precipitated with it. These two metals are separated in the same manner as manganese and cobalt.—*Comptes Rendus*, June 20, 1853, p. 1090.

PATENT.

Patent granted to E. J. Hughes, *for purifying and concentrating the Colouring Matter of Madder, &c.*

The patentee, in describing this invention, states, that instead of treating munjeet, madder, or spent madder with a moderate quantity of concentrated acid and water, turning to account the heat generated by the acid and water, and then applying steam to produce articles usually known in the trade as "guarancine" or "guaronceur," he takes concentrated acid and adds 20 to 25 per cent. of water; which mixture must be left to become quite cold. To this he adds, in a slow and careful manner (so as not to raise the temperature beyond about 125° F.), for every 100 parts by weight of the said mixture, 35 to 40 parts by weight of spent madder, or of madder or munjeet; which madder or munjeet must have been previously well washed and fermented, and then washed. The fermentation is to be effected by any of the usual processes, but not to be continued so as to reach the usual point of acid fermentation. When the aforesaid mixture forms a paste or thickish substance, it is diluted with water; after which a large quantity of cold water is immediately thrown upon it, with continuous stirring, to wash out the acid. To the last washing it is desirable that some neutralizing matter, such as chalk, soda, or other ingredient, be added, to effect the complete neutralization of the acid. The material may then be pressed, dried and ground.—Sealed Oct. 8, 1852.

THE CHEMICAL GAZETTE.

No. CCLXIV.—October 15, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Seat of the Sugar Formation in the Animal Body.

By Dr. J. Moleschott.

As is well known, Bernard (Comptes Rendus, xxxi. pp. 572, 573) has shown the existence of sugar in the liver, not only of all Vertebrata, but also in that of the Gasteropoda, Acephala and Decapods. Frerichs (article "Verdauung" in R. Wagner's Handwörterb. d. Physiol., p. 831) has confirmed these observations for the liver of man, and many animals; Van den Broek (Nederlansch Lancet, pp. 108–110) for that of dogs and rabbits; Baumert (Erdmann's Journal, liv. p. 359) for that of the fox, the dog, the cat and the sheep; and Kunde and Lehmann (Kunde, De Hepatis ranarum exstirpatione, Diss. Berolini, 1850, p. 11) for that of frogs.

I selected twelve frogs for my investigations; and notwithstanding the smallness of their livers, so much sugar appeared that it was easily shown by Trommer's test. Bernard and Lehmann regard this sugar of the liver as grape-sugar.

The question arises, Is this sugar of the liver derived from the blood, or is it formed by the liver proper? Bernard advocates the latter view, since he has thus obtained the sugar wholly independent of the food, with the Carnivora and Herbivora, with animals famished during hibernation, and with the fœtus in utero. Frerichs, Van den Broek, and Baumert have repeated these observations and confirmed them.

Still more important is the result obtained by Bernard (*loc. cit.*) and Lehmann (Erdmann's Journal, liii. pp. 214, 215), that the portal blood of the dog and horse contain little or no sugar, while the blood of the hepatic vein contains, like no other vein in the body, this substance in considerable quantity.

To these data I would add a fact of some import. If the sugar is not found in the liver, but is only strained off, as it were, by this last from the blood, then the blood of those animals whose liver had been removed would be found surcharged with sugar, exactly as the blood is filled with urea in animals whose kidneys have been removed. But with frogs, some of which had been without the liver for fourteen days, others for three weeks, I found no sugar in the blood, flesh, gastric juice, urine, nor finally in the water in which twenty-six of these animals thus mutilated had passed two days.

From all these facts, it appears to me indubitable that the sugar contained in the liver is formed by the liver itself.—Muller's *Archiv*, 1853, March, p. 86.

Remarks on the Potato Disease. *By* THORNTON J. HERAPATH.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

SIR,—Since I last addressed you on the potato disease, I have received numerous communications on the subject from different parts of England and the Continent, and have been repeatedly applied to for a full description of the changes I have proposed to introduce in the mode of cultivation now adopted, with the view of effecting the eradication of the disease. As my time will not allow me to reply separately to each of these applications, I will, with your permission, communicate the desired information through the medium of your pages. I adopt this course the more readily, inasmuch as I am satisfied that the directions I am about to convey will prove interesting, not only to the parties in question, but also to the majority of your readers.

It will be doubtless remembered that the changes just alluded to consist,—1st, in carefully drying the seed potatoes; 2nd, in steeping them in a dilute solution of the sulphate of copper; 3rd, in planting them in poor well-drained land; 4th, and lastly, in substituting for the farm-yard manure, &c., now employed, some mineral or inorganic compost.

Desiccation of the Tubers.—The apparatus employed to effect this object should consist of a large heated chamber, similar in character to the so-called "*stoving-room*" of a sugar-refinery, or of a long room fitted up with shelves for the reception of the roots, and heated by means of steam-pipes, or stoves placed at intervals, and so arranged that a current of air can be made to pass over the tubers, which can be thus rapidly and effectually dried. The same end may be attained on a small scale by exposing the potatoes in layers on the floor of a warm room, or on a maltster's kiln; precautions being taken to turn them over occasionally until they have become sufficiently desiccated, and thus promote a free circulation of the air; but in practice it will be doubtless found preferable for some enterprising parties to undertake the drying of the roots, which may be afterwards retailed to the agriculturists, &c. Great care, however, I find, must be taken in performing the operation; otherwise the vitality of the tubers is destroyed. A long-continued exposure in a dry atmosphere, at a moderate temperature, appears to afford the best results. The latter, under any circumstances, should never much exceed 110° or 112°. If the process has been well carried out, the dried roots, when rolled up in a damp cloth, or buried in the ground for a few days, will again become plump and fresh in appearance; whereas, on the other hand, if too high a temperature has been employed, they will, when thus treated, still remain comparatively hard and dry.

Steeping or Pickling Process.—Into a gallon of boiling water put a quarter of a pound of blue vitriol or blue stone (sulphate of cop-

per), and stir the solution well from time to time with a piece of stick until the salt is completely dissolved. When the temperature of the mixture has been so lowered by evaporation and exposure that the hand of the operator can be immersed without any inconvenience, the dried tubers should be thrown into the vessel containing the "*pickle*," in which they should be kept for one or two hours, care being taken to stir them well two or three times during that interval. After they have been removed from the cupreous solution and well drained, they should be dusted over with a little air-slaked or mild lime, and planted in the usual way. When, however, the drying process before described has not been resorted to, the tubers should be allowed to remain in the copper solution for thirty or thirty-six hours, and the pickle should be made of double strength.

Preparation of the Mineral Manures.—Mix intimately—

30 lbs. of wood-ashes,
15 lbs. of calcined bones, in fine powder,
10 lbs. of gypsum,
20 lbs. of common salt,
30 lbs. of air-slaked lime, and
7 lbs. of nitrate of soda.

Whilst planting the potatoes, into every hole put about ½ an oz. of the above compost; cover the latter over with some earth, and then plant the tubers in the ordinary way. This manure may be easily prepared by any one at a very trifling cost, and may be measured out by means of a small tin cup, which for convenience sake should be suspended to the waist of the dibbler. On large farms, where the roots are set in drill-furrows, the compost may be more readily distributed by the manure-drill, or by hand in the usual manner. On most soils, however, a simple top-dressing of lime and salt, in the proportion of 2 bushels of lime to 1 of salt, will be doubtless found sufficient; the manure being employed at the rate of 50 or 60 bushels per acre. Where the land is rich, the admixture of cinders, coal-ashes, or shell-sand with the soil will be found decidedly beneficial.

Further observations I shall reserve for a future occasion, when I hope to be enabled to communicate the results of some extensive experiments, as I am informed that several well-known agriculturists, amongst whom is the celebrated Mr. Pusey of Farringdon, are fully determined to carry my suggestions into practice.

I remain, Sir,
Your obedient Servant,
THORNTON J. HERAPATH.

Mansion House, Old Park, Bristol,
October 1, 1853.

Revision of previous Analyses of some Constituents of Fat. *By* Dr. J. J. POHL.

Under the above title Pohl furnishes a careful comparison of the results of the existing analyses of various fats. He has taken the

trouble of calculating the carbon in the older analyses according to the equiv. 6·00. The author places particular value upon the investigations of Heintz, and considers that it is now completely established that margaric acid is only a mixture of stearic and palmitic acids. He also admits as proved that Varrentrapp's olidic acid must be regarded, with Brodie and Heintz, as palmitic acid, and stearophanic acid also as stearic acid. By a comparison of the analyses, he arrives at the following conclusions:—

1. The formula of glycerine need not be written $C^6 H^8 O^6$, as $C^3 H^4 O^3$ answers equally well, nay even possesses more probability, if we pay no regard to the mere hypothesis that carbon only occurs in organic bodies united with other elementary bodies in even numbers.

2. Stearine is regarded, according to Duffy's most recent experiments, as a mere mixture with other salts of fatty acids. The analyses of Liebig and Pelouze, however, agree with the formulæ $C^3 H^3 O^2$, $C^{36} H^{35} O^3$.

3. Palmitic acid, reasoning from previous analyses, agrees with the formula $C^{30} H^{30} O^4$, and not $C^{32} H^{32} O^4$.

4. Japanese wax is neutral palmitate of oxide of glycyle, $C^3 H^3 O^2$, $C^{30} H^{29} O^3$.

5. The palmitonic acid of Schwartz appears, according to previous analyses, to be a mixture of palmitic acid with one or more of its products of decomposition.

6. Myristic acid does not agree with the formula $C^{28} H^{28} O^4$, but with $C^{27} H^{27} O^4$ or $C^{26} H^{26} O^4$; according to Playfair's analyses of myristine, which was not perfectly pure, its formula is $C^3 H^3 O^2$, $2C^{28} H^{27} O^3$.

7. Laurostearic acid, according to the composition of its salts, corresponds with the formula hitherto accepted, $C^{24} H^{24} O^4$; laurostearine is represented by $C^3 H^3 O^2$, $2C^{24} H^{23} O^3$, and is consequently acid laurostearate of oxide of glycyle.—*Sitzungsber. der Akad. der Wiss. zu Wien, Math. Naturw. Klasse*, x. p. 485.

On Hydrated Chloride of Magnesium, Fused and in Powder. *By* M. Casaseca.

When a concentrated solution of chloride of magnesium is evaporated to dryness, the salt is decomposed, muriatic acid is evolved, and free magnesia is obtained. Some chemists think that the decomposition is complete; and others, as Berzelius, state that nearly the whole of the acid escapes when the chloride is heated to redness.

The author has found that even after the residue of evaporation has been exposed for a quarter of an hour to a red heat, a very considerable quantity of the salt remains undecomposed. He also found that the decomposition of the salt during evaporation, commenced at the moment when a hydrate of the composition MgCl, 6HO was attained. To obtain this hydrate in a fused state, the evaporation must be stopped as soon as the vapour begins to redden blue litmus-paper. The liquid is then to be poured rapidly into a

silver basin, previously heated, which is then cooled by water, as in the preparation of caustic potash. During the cooling, the basin is to be turned in all directions, so as to get a layer of nearly equal thickness throughout; the hydrate of chloride of magnesium, when cooled, may be wholly detached from the basin, by a smart blow on a table covered with a sheet of paper. It must then be broken into pieces, and put into well-stopped bottles. If the basin be placed on a vapour-bath, the hydrate stirred with a silver spatula so as to divide it, and then triturated whilst on the bath with a porcelain or glass pestle, the salt will be obtained in powder.

This hydrate being very deliquescent, may be employed like chloride of calcium for drying gases, and will also prove otherwise useful in the laboratory.—*Comptes Rendus*, August 29, 1853, p. 350.

On a Product of the Action of Sulphuric Acid on Resinized Oil of Turpentine. By F. KUBERTH.

The resin which is formed in course of time from commercial oil of turpentine, when treated with sulphuric acid and distilled, furnishes a colourless oil, which becomes brown when exposed to the air. Its odour resembles at once that of rue and rosemary. Oil of turpentine, similarly treated, does not furnish this oil.—*Chem. Pharm. Centralblatt*, July 27, 1853, p. 480.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On MM. Leplay *and* Dubrunfaut's *Improvements in the Manufacture of Sugar. By* J. NICKLÈS.

THE manufacture of beet-sugar has for some years been largely carried on in France. In ten years the production has doubled notwithstanding the successive duties which have been imposed, duties of an excessive character, since 100 kilogrms. of white loaf-sugar pay 59 francs of duties, and sell at 150 francs. In 1842, the production of beet-sugar throughout France was about 40,000,000 kilogrms, and to-day it is 80,000,000. This progress has been owing to improvements each year in the manufacture.

Among these improvements, the most important is that called the *barytic*, introduced by MM. Leplay and Dubrunfaut, and which enables them to obtain 50 per cent. of the crystallizable sugar contained in the molasses. It is well known that for a long time these molasses were of little value. Their sugar was supposed to be wholly uncrystallizable, and their only use was for making alcohol by fermentation, for which purpose large distilleries had been constructed. In an establishment of this kind, directed by M. Leplay, 12,000 kilogrms. of the beet-molasses were consumed per day in making

alcohol of 94 per cent., which was wholly used in the manufacture of fine liquors.

MM. Leplay and Dubrunfaut were the first to recognise that the sugar in the molasses was a sugar perfectly crystallizable, and having all the characters of ordinary sugar; and that to crystallize it, it was only necessary to separate the interfering foreign substances, by operating on the juice of the beet which furnishes the molasses. The solution of the problem was one of great importance, since the amount of molasses annually produced in France was 40,000,000 kilogrms., containing more than half its weight of sugar.

Their process, as I have studied it for some years at the establishment of La Villette, near Paris, is as follows:—It is based on the insoluble compound which sugar forms with baryta. When a boiling solution of caustic baryta at 30° B. is poured into the ordinary molasses, the substances contained immediately solidify into a porous crystalline mass, insoluble in water, and admitting therefore of thorough washing.

After being thus purified, the saccharate of baryta is white, and has the appearance of a thick paste; it is exposed to a current of carbonic acid, which takes up the baryta and sets the sugar at liberty. This operation is carried on in large vats of wood, 80 to 100 hectolitres in size, into which strong pumps worked by steam inject carbonic acid, obtained by the calcination of carbonate of lime in lime furnaces.

While the reaction of the carbonic acid is going on, it is observed that the paste of saccharate, before very thick, gradually liquifies; and when complete, the whole is a solution of sugar containing carbonate of baryta in suspension.

To separate the carbonate, the mixture is put into sacks made of cotton fabric, through which the syrup filters clear, while the carbonate is retained. These sacks, after draining thoroughly, are pressed lightly in a screw-press, and then subjected to heavy hydraulic pressure, in order to extract the syrup from the carbonate. This syrup, thus obtained, marks 18° to 22° B.; it is white, of agreeable taste, and holds in solution some traces of the carbonate and bicarbonate of baryta, which may be removed by means of a sufficient quantity of plaster, or of sulphate of alumina. Finally, it is clarified by means of dried blood; it is skimmed and filtered, and boiled down like a syrup for the refinery, after which it is put into forms for crystallizing. We thus obtain at once sugar equal in quality to the finest sugars of commerce.

With regard to the residues of this process, the carbonate of baryta, saline substances contained in the molasses, quicklime proceeding from the calcination of the limestone, &c., I have learned the following facts:—The carbonate of baryta may be used an indefinite number of times; it is rendered caustic anew after each operation by mixing it with charcoal and heating it, and so it serves again. The loss of the baryta, which is unavoidable, is resupplied from sulphuret of barium, which M. Leplay prepares by calcining sulphate of baryta with 45 per cent. of charcoal in a reverberatory

furnace, and which he would prepare more advantageously still if he would apply the process suggested by Gibbs, which consists in reducing the sulphate by the gas of the refinery. The sulphuret of barium possesses equally the property of precipitating the sugar, only there are 2 equivs. of sulphur when 1 of oxygen would suffice. In fact, this last case gives—

$$\text{Sugar} + \text{BaO} + \text{HO} = \text{saccharate of BaO} + \text{HO},$$

whilst the sulphuret affords—

$$\text{Sugar} + 2\text{SBa} + \text{HO} = \text{saccharate of BaO, SH, SBa}.$$

There is hence lost 1 equiv. of sulphuret of barium. To avoid this loss, 1 equiv. of potash, or caustic soda is added to the molasses under trial; and then, on pouring in the sulphuret of barium, all the baryta is precipitated in the state of saccharate, and the liquid retains the potassium in the state of a hydrosulphate.

$$2\,\text{sugar} + 2\text{SBa} + \text{KO} + \text{HO} = 2\,\text{saccharate of BaO} + \text{SH, SK}.$$

The use of caustic potash produces a residue with carbonic acid, like the quicklime, and would be too expensive for the purpose were it not regenerated with each operation. In fact, the waters after washing are collected in boilers, evaporated, and the product then calcined in a reverberatory furnace with some chalk or lime, and fused. The fused substance is cooled, broken up, lixiviated, rendered caustic by means of lime, and the leys are concentrated as in the manufacture of soda. The potash is thus obtained for a new precipitation of the saccharate.

In this operation, they obtain not only the potash added in the process, but also the potash and soda which existed primarily in the juice of the beet, and which, by accumulation in the molasses, amounts to about 10 per cent.

In this manner MM. Leplay and Dubrunfaut have succeeded in isolating œconomically the sugar of beet-molasses. But is this process applicable to the extraction of cane-sugar? Yes, on one condition; that is, if the manufacture of cane-sugar can be so conducted as to give molasses free from uncrystallizable sugar. For MM. Leplay and Dubrunfaut have shown that for 60 to 70 per cent. of sugar in the molasses, there are 30 per cent. of uncrystallizable sugar, which is a result of the method of manufacture, and not pre-existent in the juice of the cane.

There exists then great differences between the manufacture of beet-sugar and cane-sugar; in the former the molasses contain no altered sugar, and in the latter there is a large quantity of altered sugar.—Silliman's *Journal*, September 1853.

Manufacture of Caustic Baryta from the Carbonate.
By MM. Leplay *and* Dubrunfaut.

We have mentioned above the general process by means of which MM. Leplay and Dubrunfaut reduce the carbonate of baryta. The point is important, and we add some further details; for it has

required much time and experiment to accomplish it conveniently on a large scale. The process is now so far perfected, that caustic baryta may be obtained at a very low price.

After reducing the carbonate to powder, it is mixed intimately with 20 to 25 per cent. of pulverized charcoal, and then put in a reverberatory furnace made of good refractory brick. At a reddish-white heat the reduction commences, and the aspect of the mass shows when it is complete. A single furnace will thus reduce in twenty-four hours 1200 kilogrms. of carbonate of baryta, consuming 12 hectolitres of charcoal in heating, and 4 hectolitres for the reduction. Three workmen are required. When finished, the baryta is collected in metal cases ("*étouffoirs*," large sheet-iron boxes holding about 1 hectolitre), in which it is cooled. The artificial carbonate is usually reduced more easily than the native. However, the native carbonate from England is easily decomposed.—Silliman's *Journal*, September 1853.

Cheap Red Fire.

3 parts of powdered celestine, 2 parts of sulphur, and 3 parts of chlorate of potash.—*Jahrb. für Prakt. Pharm.*, xxvi. p. 321.

ANALYTICAL CHEMISTRY.

On the Analysis of Cast Iron.

By Professors Campbell Morfit *and* James C. Booth.

[Continued from p. 378.]

Calcium, Magnesium, Sodium, Potassium, Cobalt, Nickel, Iron, Manganese, Aluminium, Copper and Phosphorus.

Another portion of metal is required to be digested for the estimation of these components, because the filtrate from the carbon, by digestion with iodine, does not contain all the phosphorus and alumina, as has already been stated. The filtrate from the digestions in hydrochloric acid for allotropic carbon and for silica and slag have also lost a portion of their phosphorus, which during the digestion passed off as phosphuretted hydrogen gas. Moreover, some of the above constituents are in such small proportions, that they cannot be determined in 1 grm., the quantity used in the forementioned digestions. The proper course therefore is to proceed as follows:—

5 grms. of clippings of metal are placed in a beaker of 8 oz. capacity, drenched with fuming nitric acid, covered, and set aside in a cool place; for if heated immediately, the reaction would be so violent as to eject particles. After twelve hours, pure nitric acid is added, and the beaker transferred to the extreme end of the sand-bath, so that it may not be subjected to a higher heat than 212° F., as phosphoric acid will volatilize above that temperature from solutions containing free acid.

When the solution is perfect, as may be known by the flocculent appearance of the insoluble particles, the cover is removed, and the liquor allowed to evaporate gradually to dryness. Hydrochloric acid is added, the cover replaced, and digestion continued until re-solution is effected.

The addition of hydrochloric acid is necessary to ensure the entire solution of all the oxide as well as basic salt which are formed by the nitric acid, but are insoluble in it or in water alone; besides, some phosphide of iron, which can only be entirely dissolved in hot *aqua regia*, may otherwise remain, because of its insolubility in nitric acid alone. Hydrochloric acid alone would not answer; for, as before stated, it would dissipate most of the phosphorus as phosphuretted hydrogen gas.

By this prolonged treatment, which, if pursued as we have directed, causes no loss of phosphoric acid, the iron, chrome, manganese, aluminium, calcium, magnesium, sodium, potassium, cobalt, nickel, and copper are entirely dissolved, and remain in the liquid; while the subsident matter contains part of the carbon, all the silex and slag, together with tin and titanium, as oxides, if the latter are present in the metal. It is requisite that the hydrochloric acid used in the re-digestion be strong; otherwise the alumina, which loses its acid by evaporation, becomes re-soluble with difficulty. As dense metallic solutions, particularly when acid, are apt to clog the filter, the liquid is next to be diluted with water, so as to facilitate the filtration, then filtered through fine paper, and well washed with hot water. The filtrate is A, the filter *a*. The latter is set aside for subsequent treatment for tin and titanium.

To the filtrate A, aqua ammoniæ free from carbonate is added in excess. Alumina, and the oxides of chrome, manganese and iron, with phosphoric acid, are precipitated; while lime, magnesia, cobalt, nickel, copper, sodium, and potassium remain in solution. The presence of ammonia in excess holds up the copper, cobalt and nickel; and that of ammoniacal salts, as a general rule, also retains the manganese in solution as well as the magnesia; but where the iron with which the manganese is associated is so largely in excess, as in the present instance, the latter is wholly precipitated with the former. Of numerous essays, there are very few in which even traces were left. If the solution is not acid previous to the addition of aqua ammonia, some muriate of ammonia must be added. Immediate filtration should always follow the treatment with aqua ammoniæ, to avoid the transfer of carbonic acid from the air to the lime, and the consequent precipitation of carbonate of lime. The filter is well washed with hot water, and set aside as *b* for the present.

Calcium.—The filtrate B will have a bluish tinge if any copper is present, and is to be evaporated to a dense solution, mixed with twice its volume of absolute alcohol, and the lime precipitated by a few drops of sulphuric acid. The sulphate of lime is filtered off, washed with dilute alcohol, ignited, weighed, and the amount of calcium calculated from the sulphate.

The filtrate from the lime is then evaporated very cautiously to

dryness, and heated to expel every trace of ammoniacal salt. In case the sulphuric acid should be in excess, it is well to neutralize it with a piece of carbonate of ammonia, to be added after the evaporation and previous to the heating, which must be to slight redness, and continued until the weight of the crucible and contents remains constant. This expresses the weight of the sulphates of potash, soda and magnesia, with traces of copper, cobalt and nickel, if they should be present.

The saline mass is dissolved in water, and the solution divided into two equal portions. In the analyses of some silicates, a small insoluble residue is apt to be left in making this solution, and it chiefly consists of manganese and silica; but in the present analysis such residue is not observed.

One portion of the solution is treated with chloride of barium, to precipitate sulphate of baryta, from the weight of which, the sulphuric acid, doubled, expresses the whole amount of this acid in the joint weight of the sulphates above determined. The excess of baryta being removed from the solution by sulphuric acid, sulphuretted hydrogen is passed through the solution, whereby sulphide of copper, if present, is precipitated.

Copper.—The sulphide of copper and sulphate of baryta are filtered off, and the copper determined, if necessary, by re-solution of the sulphide in nitromuriatic acid, after removal from the paper, and by precipitation when boiling by potash. The solution filtered from the sulphide of copper is tested for cobalt and nickel by adding ammonia and a few drops of sulphide of ammonium, and then acidulating carefully with hydrochloric acid; a black sulphide remaining, indicates cobalt or nickel, and may be further tested; but we have hitherto only found traces of these metals in the present analyses.

Magnesium.—The second portion of the solution of joint sulphates is treated with ammonia and phosphate of soda, whereby the ammonio-phosphate of magnesia is thrown down; it is filtered, washed with ammoniacal water, dried, burned off, and the amount of magnesium calculated from the weight of the phosphate of magnesia, which is to be doubled.

Potassium and Sodium.—Having determined the magnesia and the total amount of sulphuric acid in the joint sulphates, the relative amounts of potash and soda may be calculated by indirect analysis or by a simple equation; by calculating the amount of sulphuric acid required by the magnesia, which happens to be just twice its weight, and subtracting this from the total amount of sulphuric acid in the joint sulphates, we have the amount of sulphuric acid, s, combined with the alkalies. Further, by subtracting the weight of the sulphate of magnesia from that of the joint sulphates, we have the weight of the alkaline sulphates, from which, if their sulphuric acid be taken, the remainder is the joint weight a of the alkalies. Then $2{\cdot}9186\,a - 2{\cdot}258\,s$ = the weight of potash. This subtracted from a gives the weight of soda. The metals potassium and sodium are calculated from the weights of their oxides. This method of indirect

analysis we have found practicable when the quantities to be weighed are such as to throw the errors of observation into the hundredths' place, and when there is not too great a preponderance of one alkali. When the traces of alkali are very minute, Andrews's method (Chem. Gaz., 1852, p. 378), by means of the polariscope, is very useful for determining whether they consist of potassium and sodium jointly, or either of them singly.

In our first essay, we separated the lime from filtrate B with oxalate of ammonia, filtered it off, evaporated the filtrate in a porcelain capsule, under paper cover to avoid dust, ignited to expel ammoniacal salts and chlorine from magnesia, and towards the end added a little oxide of mercury, to ensure the expulsion of the last trace of chlorine that might remain, and again heated to redness, to drive off excess of mercury. The magnesia was thus oxidized and rendered insoluble, while the residual components remained soluble. The capsule and contents having been weighed and the weight of capsule deducted, the remainder was noted as the gross weight of magnesia, alkalies, cobalt and nickel. The latter three being as chlorides, the proportion of radicals was calculated accordingly.

The presence of cobalt, and probably nickel, was recognised in this method, by the pink tinge in the evaporated saline mass; but their quantity was too small to be determined. The soluble matters were dissolved out by hot water, and the insoluble magnesia separated by filtration, dried, ignited and weighed; its weight, deducted from the gross weight of the magnesia and alkaline chlorides, gave the amount of the latter, whence was calculated their proportion of radicals.

It is very difficult, even with the most skilful manipulation, to prevent a partial volatilization of the alkaline chlorides at the temperature necessarily used in the ignition, especially in a current of air and where a quantity of ammoniacal salt is sublimed, but yet it has hitherto proved the more accurate method*. Since, however, the quantities of alkali in these analyses proved exceedingly small, we preferred the former process, and determined only the joint amount of potash and soda.

The contents of filter *b*, consisting of oxides of manganese, chrome and iron, with alumina combined with phosphoric acid, are carefully transferred from it with a porcelain spatula to an 8 oz. beaker glass; the filter is washed with hot water, dilute hydrochloric acid, and lastly with hot water, to remove every trace of iron solution that may be retained in the pores of the paper.

This process of solution by displacement of the portions of iron adhering to the filter saves time, trouble and loss, as it reduces the number of filtrations which would otherwise be necessary if the filter with its contents had been jointly digested.

The filter containing nothing is rejected. The filtrate, holding in solution the entire contents of the filter, is to be neutralized with aqua ammoniæ, and then treated with a slight excess of hydrosul-

* The recent method of Lawrence Smith (Chem. Gaz., p. 257 of the present volume) is an important improvement in the removal of ammoniacal salt.

phide of ammonium, and immediately afterwards with 2 fluid drachms of caustic potash solution of spec. grav. 1·30. All the iron as well as manganese precipitates as sulphide, but the alumina and chrome are retained in solution by the potash. As soon as the precipitate has wholly subsided, but not until then (and it is therefore well to promote the separation by gently warming the liquor upon the ledge of the sand-bath), the clear supernatant liquor is filtered off, and 6 fluid drachms of caustic potash solution of 1·30 added to the sediment, and the whole digested for a few minutes on the sand-bath to ensure the removal of every trace of alumina and phosphate. It is then diluted with water, filtered on the same filter as employed for the first liquid, and washed with dilute hydrosulphide of ammonium, to prevent the formation of soluble sulphate of iron by the action of air and water. The filtrate is C and the filter *c*.

Manganese.—The filter *c* contains iron and manganese as sulphides, and its contents must be digested in nitric acid, filtered and washed, to separate any unoxidized sulphur. Hydrochloric acid cannot be substituted for the nitric, as it is absolutely necessary that all the iron shall be in a state of peroxidation, because, if any of it is protoxide, it remains in solution with the manganese, and leads to error. If the potash was not entirely removed from it by hot washing previous to the digestion, it will now exist in the liquor as sulphate and nitrate, and being an impediment to the after-steps of the process, must be removed. This is done by precipitating the iron and manganese by ammonia, washing with hot water, and redissolving in hydrochloric acid. When the solution has become cold, it is ready to be treated for the separation of the manganese from the iron, which is accomplished by adding a slight excess of pure carbonate of baryta portionwise, setting aside for twelve hours at the ordinary temperature, and stirring occasionally during the interval. When the reaction is completed, all the iron has precipitated, while the manganese remains in solution. The whole is to be filtered and washed with hot water. The filtrate is D and the filter *d*. The filtrate D is frequently cloudy, owing to the intimate suspension of particles of carbonate of baryta and iron precipitate which passed through the filter; and these must be separated, to prevent their contaminating the manganese by after-solution in acid. The solution is therefore evaporated to one-fourth its volume, and the suspended matters, whose subsidence is thus effected, filtered off and added to the filter *d*. The evaporation answers the double purpose of concentrating the liquor sufficiently to ensure the entire separation of the baryta salt, which is then removed by the addition of sulphuric acid, filtering, and washing with hot water. The filtrate is further evaporated under paper cover, tested with a drop of sulphuric acid, to be assured of the absence of baryta, and treated with a clear solution of carbonate of soda in slight excess. The whole is well warmed in the sand-bath, the precipitated manganese filtered off, washed with hot water, ignited until the weight remains constant, and the amount of metal deduced by calculation. The manganese is precipitated as carbonate; but when highly ignited in

contact with air, like all the other oxides of manganese, it becomes manganosomanganic oxide (MnO, Mn^2O^3). To reach this state, it requires prolonged heating, and consequently the ignition and weighing must be repeated twice or thrice, as may be necessary, to ascertain when this condition is reached.

Iron.—The contents of filter *d*, consisting of pure oxide of iron with excess of carbonate of baryta, are transferred with a platinum spatula to a glass beaker, and the traces adhering to the filter displaced by hydrochloric acid and hot water, as directed before. After digestion with a little more hydrochloric acid until solution is complete, sufficient sulphuric acid is added to precipitate all the baryta salt as sulphate, which is then filtered off. Before filtration it is better to allow repose, so that the precipitate may subside and leave a clear supernatant liquor. This passes the filter very readily; and when all of it has gone through, the pasty residue should be drenched with hot water, poured upon the filter, and washed with hot water. The filtrate is less apt to be cloudy by this mode. A drop of sulphuric acid is to be added to the filtrate to obtain assurance that there is no baryta retained in the solution. Beakers should be exclusively used as containing vessels in these separations of baryta, for glass shows much more readily than porcelain whether any suspended particles cloud the filtrates.

As the sulphate of baryta, precipitated from the iron solution, tenaciously holds a portion of the latter, the former must be well washed on the filter, first with hydrochloric acid, and then with hot water.

The consecutive addition of hydrochloric and sulphuric acids to the contents of filter *d* is much better than the seemingly shorter plan of adding sulphuric acid direct and alone to the filter, and displacing the iron as soluble sulphate, while the insoluble sulphate of baryta remains upon the paper. The latter mode endangers the carbonization of the filter, and the introduction of soluble organic matter into the liquid, which would in a subsequent stage prevent the entire precipitation of the oxide of iron.

The clear iron solution, freed from baryta, is to be treated with aqua ammoniæ in slight excess, and the precipitated oxide of iron filtered off and washed well with hot water; the filter is then thoroughly dried in the air-chamber, its contents detached, and the two ignited separately in a platinum crucible, to prevent reduction of oxide by the carbon of the filter. The metallic iron is then calculated from the weight of Fe^2O^3.

Our experience proves that manganese is separated from iron in a satisfactory manner by carbonate of baryta, but certain precautions are necessary to success.

At least twelve hours must be allowed for the precipitation of the iron after the addition of the carbonate of baryta, and to be satisfied that all has gone down, it is better to test a drop of the clear supernatant liquor with sulphide of ammonium.

As sulphate of baryta is very liable to pass through the filter, care must be taken in every such event to promote its deposition by warmth and repose, and to separate it by re-filtration.

Manganese is generally separated from iron, when there are no other associates, by carefully neutralizing the hydrochloric solution of the two with aqua ammoniæ, and then adding succinate of ammonia, the first to retain the manganese in solution, while the latter precipitates the iron. But when the iron is largely in excess, it is impossible to prevent the manganese going down wholly, or nearly so, with it, even although the exact point of neutralization by ammonia, a very nice manipulation, is attained previous to adding the succinate. Besides, the wash-water, especially if warm, may induce the formation of soluble acid succinate of iron, and carry away a portion of it through the filter. In the ignition of the succinate, there is also a difficulty in preventing the carbon of the succinic acid reducing a little of the oxide of iron when the quantity of the succinate of iron is large. This latter objection may however be partially obviated by washing the filter with cold ammonia instead of hot water.

Herschel's method with carbonate of ammonia, founded upon the fact that $Fe^2 O^3$ of the neutral persalts of iron is precipitated from the solutions of these salts by boiling, whilst oxide of manganese remains in solution, and Scherer's, with caustic potash, which is a modification of it, have also the disadvantage of requiring difficult manipulation and very exact pre-neutralization to ensure the precipitation of the one and the retention of the other (Rose, ii. 93).

Henry's process (Journ. de Chim. Méd., 1850), without yielding any more accurate results than the carbonate of baryta plan, is tedious and time-consuming; moreover, as organic matter is used, the manganese may be partly retained in solution as protoxide, and its correct estimation subsequently prevented.

The filtrate c contains the greater part of the phosphoric acid in combination with the potash which was added with the hydrosulphide of ammonium; the remainder, which is a very minute portion, is, with the alumina as a very basic compound, held in solution by the potash.

In most of the processes heretofore followed by chemists in the analysis of cast iron, the obstinate affinity of phosphoric acid for alumina has been overlooked, and that portion of it combined with the alumina, owing to the difficulty of separating it, disregarded in the determination of phosphorus.

If any excess of hydrosulphide of ammonium was added, it remains in the filtrate, and the latter must therefore be digested with nitric acid for some hours below 212° F., to expel ammoniacal salt and promote the subsidence of unoxidized sulphur, which after twelve hours' repose must be filtered off. It is not advisable to take the shorter method, after adding the acid to separate sulphur, and pour in aqua ammoniæ to throw down alumina with the sulphur, hoping to expel the latter during ignition, for sulphur first precipitated redissolves under these circumstances; care must also be observed to keep the heat always below 212° F., or there will be loss of phosphoric acid by volatilization.

After the sulphur is separated by filtration, the filtrate is to be

treated with a slight excess of aqua ammoniæ, the vessel covered with paper, and heated upon the sand-bath; after a time cloudiness ensues, and alumina falls down, and must be filtered off, washed with hot water, and set aside as *e*; the filtrate is E.

Phosphorus.—The filtrate E contains only alkaline phosphates, and after being supersaturated with hydrochloric acid, is then to be treated with a nitric solution of 0·5 grm. of fine iron wire, carefully precipitated by aqua ammoniæ, filtered, the filter washed with hot water, dried and ignited (paper separately), and weighed. The excess of weight over the amount of Fe^2O^3, that 0·5 grm. of iron should form by solution in nitric acid, is the amount of phosphoric acid which the quantity of phosphorus in the filtrate makes. Hence the latter may be deduced by calculation.

To separate the remaining traces of phosphoric acid from the aluminous precipitate, the latter must be dissolved in hydrochloric acid, and treated with tartaric acid until the solution ceases to give any precipitate by aqua ammoniæ. The tartaric acid prevents the precipitation of the phosphate of alumina by the ammonia. When barely supersaturated with aqua ammoniæ, a solution of sulphate of magnesia is added, containing so much of muriate of ammonia as will prevent the precipitation of the magnesia by the caustic ammonia. The magnesia carries down the phosphoric acid as triple phosphate from the alumina, the solubility of the latter being promoted by the tartaric acid; after several hours' repose it is filtered, washed with ammonia water, dried, ignited, weighed, and the amount of phosphorus calculated. It is added to that obtained from filtrate E.

Aluminium.—The alumina is next determined by evaporating the filtrate to dryness, burning off to charcoal, fusing the balance with bisulphate of potash to destroy the remaining carbon and render the alumina soluble, redissolving in hydrochloric acid, precipitating by carbonate of ammonia, washing with water, igniting and weighing.

Where a larger quantity of phosphoric acid and alumina is to be separated, it is a safer plan to redissolve the alumina, and treat it again in the same way with tartaric acid, magnesia, &c., but we have not found it necessary in the present analysis. The alumina obtained is tested for chrome.

This method has been found to give the most reliable results. The separation of phosphoric acid from iron alone may be readily effected by several methods; but when alumina is an associate of the iron, then the task is very difficult, owing to the similarity of behaviour of alumina and its phosphate to reagents, the affinity of phosphoric acid for alumina being very obstinate.

The process at first followed by us with great confidence was that of Berzelius, with some modifications by Rose and ourselves, and we only abandoned it after numerous and repeated essays had convinced us of its unreliability. The iron, after the separation of the manganese and every other component except phosphoric acid and alumina, was dissolved in hydrochloric acid, supersaturated with carbonate of soda, evaporated to dryness, transferred to a platinum

crucible, mixed intimately with 2 parts of impalpably fine and pure silex, and 6 parts of carbonate of soda to every 1 of phosphate, and the whole highly heated to fusion for half an hour.

The silica is added to detach the phosphoric acid from the alumina, while a part of the carbonate of soda combines with it at the moment of elimination to form phosphate of soda. The remainder of the carbonate of soda unites with the excess of silica. There are two affinities simultaneously exercising their preference; and thus the phosphoric acid, as soon as eliminated by the silica, which unites in turn with the alumina it has displaced, is embraced by the carbonate of soda. Carbonate of soda alone would not answer; for though it will by *fluxing* remove phosphoric acid from iron, it does not separate it from alumina.

After fusion, the fluxed mass was emptied from the platinum crucible into a silver capsule, and repeatedly boiled with water, filtered after each boiling, and the several liquors or filtrates united; the filter 1 contained the oxide of iron and alumina, with free and combined silica; the filtrate 2 held in solution the phosphorus as phosphate of soda, the excess of carbonate of soda, and some silicate of soda formed during the fusion.

The contents of the filter 1 were digested with hydrochloric acid for solution, then evaporated to dryness to render silica insoluble, redigested in hydrochloric acid, diluted, filtered and hot-washed. The iron and alumina were in the filtrate, and the silica remained upon the filter, and was discarded. It is unadvisable to throw the filter and its contents together into the beaker, for hot digestion with acid renders a portion of the organic matter of the paper soluble, and thus makes the subsequent precipitation of the iron imperfect. It is much better to remove the iron from the filter with a platinum spatula, and to displace the adhering traces with hydrochloric acid and hot water, as directed in a previous page. The paper filter would then be thrown away, as the washing with acid and water removes every trace of iron and alumina.

The filtered liquor was boiled in a silver capsule with a slight excess of caustic potash solution, filtered, and washed with hot water. To remove the potash obstinately retained by the iron on the filter, the latter was redissolved in hydrochloric acid, precipitated by aqua ammoniæ, filtered, thoroughly washed with hot water, and dried. The paper and contents were ignited separately and weighed.

The filtrate which contained the aluminate of potash was supersaturated with hydrochloric acid, and then treated with carbonate of ammonia, which threw down alumina as well as the silicic acid that remained in the liquid as soluble silicate. After filtration, the two were separated by digestion in hydrochloric acid, and evaporation to dryness, which left the silica and dissolved the alumina. The latter was then precipitated from the filtered solution by carbonate of ammonia, dried, ignited and weighed.

Now even at this stage of the process there is a serious objection; in the first place, during the fusion with carbonate of soda, a por-

tion of the iron, as well as of the alumina, will inevitably unite with some of the silica to form a slag insoluble by subsequent digestion in acid, thus giving rise to an error in the estimation of both these ingredients. Moreover, the boiling with carbonate of soda may have caused the solution of traces of free alumina as well as of phosphate, either of which is partially soluble in a dense solution of carbonate of soda. These being passed into the phosphate filtrate, serve to contaminate it.

The contents of the filter 1 having been estimated, the filtrate 2, containing phosphate and silicate of soda with excess of carbonate of soda, was neutralized with hydrochloric acid to remove carbonate of soda, and then treated with a given weight of fine iron wire dissolved in nitric acid. The phosphoric acid was then precipitated with the iron by caustic ammonia, redigested in hydrochloric acid, and evaporated to dryness to remove any silica that might have fallen with the phosphate and oxide of iron, and the latter was then reprecipitated from the filtered solution with aqua ammoniæ.

The evaporation to dryness, as above directed, was very necessary, as some silica invariably goes down, but the quantity is in proportion to the density of the solution; the more dilute, the less is the quantity of silica which precipitates. The evaporation of the iron solution with hydrochloric acid endangers the volatilization of the phosphoric acid, and prolongs the process; and we therefore endeavoured to provide against these drawbacks by igniting the mixed precipitates of phosphate and oxide of iron and silica, weighing, redigesting the calx in hydrochloric acid, filtering, washing with hot water, drying, and igniting the insoluble residue, and estimating the oxide of iron and phosphoric acid by loss. But there was almost invariably a fusion of a portion of the iron and silex into insoluble slag, and a serious loss thus occasioned. Rose proposes (Chem. Gaz., viii. 20) to precipitate the silicic acid from the filtrate containing the soluble matters of the fluxed iron, alumina, &c., directly by carbonate of ammonia. We do not think that this gives a reliable result; for even if the solution were very dense, the precipitated silex would be in a gelatinous state, and consequently soluble in the water used for washing. Therefore when the filtrate, after neutralization by hydrochloric acid, is treated according to Rose's directions with sulphate of magnesia to precipitate triple phosphate, a portion of silica goes down with it. This fact was ascertained by digesting the ignited ammoniophosphate of magnesia in hydrochloric acid, which left in every essay an insoluble residue of silicic acid. It was also observed, that during this digestion a part of the phosphoric acid was volatilized, as free magnesia existed in the solution.

We sought to obviate these difficulties by evaporating the phosphate filtrates to dryness, before neutralizing the excess of carbonate of soda with hydrochloric acid; but we found it impossible to render all the silica insoluble in this way, although it prevented the volatilization of the phosphoric acid. We therefore neutralized the filtrate in its *dilute* state with hydrochloric acid, added a nitric solution of a given weight of fine iron wire, and proceeded as already

mentioned in the preceding page, and with the same unsatisfactory results.

Rose was the first to note that phosphoric acid was volatilized from acid solutions of phosphates by heat, and the confirmation of the fact by ourselves was soon after reaffirmed by some conclusive experiments by Bunce (Chem. Gaz., vol. ix. p. 215), which show the loss to vary from 8 to 50 per cent.

The process which we give in a former page is a slight modification of Otto's, and has the support of our experience in favour of its being the most reliable for these investigations. It differs favourably from others in permitting the entire separation of phosphoric acid from alumina, as well as other associates, and also in requiring fewer digestions with acid, and in prescribing a limitation of the temperature to 212° F., and thus preventing as far as possible any loss of phosphoric acid by volatilization. The only inconvenience attending it is burning off a large amount of tartaric acid, and the separation of the alumina from the excess of magnesia added.

Fuchs has given a method (Rose, ii. 438), by which the silica, instead of reacting by fusion, is added to a hydrochloric solution of the oxide of iron, alumina and phosphoric acid, in the state of liquid silicate of soda. Ulgren (Journ. Pract. Chem., liii. 27) amended it by substituting a mixture of silicate of soda and sulphide of potassium, so that the iron may be precipitated as sulphide, the alumina as silicate, and the phosphoric acid remains in solution with the alkali. This is a very ingenious process, but is no less tedious than Rose's, and is moreover equally objectionable in other respects, from a liability of loss of phosphoric acid and alumina, owing to the repeated digestions required to isolate them from silica, &c. There is also a more recent method of the same chemist (Chem. Gaz., 1851), based upon the permanent solubility of the ammoniophosphate of magnesia in small quantities of ammoniacal solution of tartrate of iron, but not in ferridcyanide of potassium—tartaric acid and cyanide of potassium being the reagents employed. It may yield correct results, but it has no advantage over Otto's plan as to time and easiness of execution.

Reynoso's method of separating phosphoric acid by oxide of tin (Chem. Gaz., ix. 418), appearing only to have been tried with an alkaline phosphate, we have not thought it necessary to devote the time required to determine its applicability to an aluminous compound, since we found Otto's plan all-sufficient for our purpose.

[To be continued.]

On the Reduction of Arsenic and Antimony by Means of Cyanide of Potassium. *By* H. Rose.

The author has carefully investigated the behaviour of antimony and arsenic towards cyanide of potassium, in order to ascertain in what cases in analytical chemistry these reductions may be performed with certainty.

Arsenic, when reduced by fusion with cyanide of potassium, becomes volatilized. In consequence of this ready volatilization of the metal, its quantity cannot be exactly determined; in qualitative in-

vestigations, however, cyanide of potassium has long been employed for the purpose of showing the presence of this metal, even in compounds in which it is difficult of reduction by other means.

Both the sulphurets of arsenic, AsS^3 and AsS^5, when fused in the smallest quantities with cyanide of potassium in a glass tube, give a spot of metallic arsenic. Sulphocyanide of potassium is formed, but cyanide of potassium does not reduce and volatilize the whole of the arsenic from the sulphuret. A sulpho-salt of arsenic is produced, which resists decomposition by cyanide of potassium. Consequently if the fused mass be dissolved in water, diluted acids throw down yellow sulphuret of arsenic from the solution, with evolution of sulphuretted hydrogen.

If, therefore, sulphuret of arsenic be mixed with sulphur, no arsenic is separated, or metallic spot produced by fusion with cyanide of potassium.

Moreover, the presence of readily-reducible metals may hinder the sublimation of the arsenic, and prevent the separation of a portion or of the whole of it. The arsenic separates at the same time with the other reduced metals, forming with them an arseniuret, from which a portion of the arsenic can be sublimed in the metallic state only when that metal is present in excess.

When arsenite of copper (Scheele's green) is fused with cyanide of potassium, only a small spot of metallic arsenic is obtained. If the copper salt be intimately mixed with more oxide of copper, and the mixture be then fused with the cyanide of potassium, no trace of arsenic is obtained.

If arseniate of soda be mixed with an excess of lead, and then fused with cyanide of potassium, the whole of the arsenic is reduced together with the lead, but no sublimate of arsenic is produced.

The fusion of arseniate of lead with cyanide of potassium furnishes much reduced and sublimed arsenic. But if the salt be previously mixed with a considerable quantity of oxide of lead, no arsenical spot can be obtained by fusion with cyanide of potassium.

When finely-divided sulphuret of lead, mixed with sulphuret of arsenic (AsS^5), is fused with cyanide of potassium, a faint arsenical spot is obtained, even when the sulphuret of lead is present in considerable excess. But if the sulphurets of lead and arsenic be first fused together, or only heated sufficiently to cause them to cake, fusion with cyanide of potassium produces no arsenical sublimate.

The production of sublimed arsenic is also prevented when arseniate of soda is fused with cyanide of potassium, and with a very large quantity of oxide of silver, with gold or the oxides of iron, nickel and cobalt.

If, on the other hand, a mixture of oxide or protoxide of manganese with arseniate of soda be submitted to fusion with cyanide of potassium, a strong spot of sublimed arsenic is obtained. The cyanide of potassium does not reduce oxide of manganese by fusion with it.

From the same cause, moreover, a dark arsenical spot is produced when arseniate of soda, mixed with much oxide of zinc, is fused with cyanide of potassium. Nevertheless an alloy of zinc

with a little arsenic furnishes no metallic arsenic when fused with cyanide of potassium.

Oxide of bismuth, also, when mixed in very large quantity with arseniate of soda and cyanide of potassium, has no power to prevent the volatilization of the reduced arsenic, although the oxide of bismuth is completely reduced in the operation. The affinity of bismuth for arsenic is however so weak, that the arsenic may be expelled from an alloy of bismuth and arsenic by the simple application of heat.

But there is no metal from which arsenic is so completely separated by mere heating, as from antimony. On this account a very small quantity of arsenic contained in compounds of antimony can be discovered by no other means with so much certainty as by fusion with cyanide of potassium. The smallest quantity of arsenic is volatilized after the reduction, and none of it remains with the antimony which has been reduced simultaneously with it.

A very small quantity of sulphuret of arsenic contained in sulphuret of antimony may be easily discovered by means of cyanide of potassium. The author, however, shows completely why the presence of arsenic is not to be discovered in this manner in the crude antimony of commerce, which almost always contains small quantities of sulphuret of arsenic.

In the compounds of arsenic acid with the alkalies, the alkaline earths, magnesia and alumina, the arsenic may be readily reduced, and obtained in metallic spots, by means of cyanide of potassium.

Antimony.—The antimony is completely reduced from the antimoniates of the alkalies by fusion with cyanide of potassium; on the solution of the fused mass in water, nearly the whole of the antimony is obtained in a large ball, only a small quantity being separated in a pulverulent form. The reduction of this metal by means of cyanide of potassium cannot however be employed in quantitative analysis, as a small quantity of it becomes volatilized during fusion. This probably takes place in the form of antimoniuretted hydrogen, in consequence of moisture in the cyanide of potassium.

From sulphuret of antimony, also, in all its modifications, the antimony is reduced by fusion with cyanide of potassium, although not completely. Sulphocyanide of potassium is formed. But if the fused mass be dissolved in water, and the filtered solution supersaturated with dilute muriatic acid, red sulphuret of antimony is separated, with evolution of hydrocyanic acid and sulphuretted hydrogen gas. During fusion, sulphocyanide of potassium is formed, together with a sulpho-salt of antimony, from which the antimony cannot be reduced by cyanide of potassium.

From one sulpho-salt of antimony, namely the well-known compound of sulphuret of antimony and sulphuret of sodium ($3NaS + SbS^5$), no antimony is consequently separated in a metallic form by means of cyanide of potassium. Neither is this separation effected when an alkaline carbonate and antimoniate, sulphur, and cyanide of potassium are fused together.—*Bericht der Akad. der Wiss. zu Berlin*, 1853, p. 441.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Transformation of Tartaric Acid into Racemic Acid, the Discovery of Inactive Tartaric Acid, and a new Method of separating Racemic Acid into Dextro- and Lævo-tartaric Acids. By L. PASTEUR.

IN a memoir recently presented by me to the Academy of Sciences*, I showed that all the salts of cinchonine, of quinine, of quinidine and of cinchonidine, when submitted to the action of heat, were capable of being converted into salts of quinicine and cinchonicine, two new organic bases, isomeric respectively with quinine and quinidine, and with cinchonine and cinchonidine. If, in the study of these isomeric metamorphoses, the tartrates of these alkalies be employed, and the action of heat be carried far beyond the point at which cinchonicine and quinicine are produced, the modifying influence of the heat is exerted upon the tartaric acid itself. Thus tartrate of cinchonine, submitted to a gradually-increasing temperature, becomes first of all converted into tartrate of cinchonicine. When the heat is continued, the cinchonicine becomes changed; it loses water, acquires a colour, and becomes converted into quinoidine. The tartaric acid also undergoes important modifications, and after five or six hours' exposure to a heat of 338° F., a portion of it has become changed into racemic acid. The vessel is then broken, and the black resinous mass contained in it treated repeatedly with boiling water; the liquid is filtered after cooling, and chloride of calcium added to it in excess, by which all the racemic acid is immediately precipitated in the form of racemate of lime, from which the racemic acid is readily extracted.

The principal part played by the cinchonicine in this operation, is to give a little stability to the tartaric acid, and to enable it to support, without destruction, a temperature which would change it rapidly in a free state. Cinchonine and cinchonicine, although they are substances which act upon polarized light, play no part in this transformation. Tartaric æther, for example, in which tartaric acid is in combination with an inactive body, which is capable of supporting an elevated temperature without destruction, furnishes considerable quantities of racemic acid by the action of heat.

The racemic acid thus artificially obtained is completely identical,

* Chem. Gaz., 1853, p. 321.

both in its physical and chemical properties, with natural racemic acid. It especially possesses the important character of being capable of resolution into dextro- and lævo-tartaric acids, exhibiting equal rotatory powers in opposite directions in their combinations with bases.

This resolution of artificial racemic acid into dextro- and lævo-tartaric acids, leads us to this result,—that ordinary dextro-tartaric acid may be artificially converted into its opposite, lævo-tartaric acid; a result which is particularly remarkable in connexion with this extraordinary fact, which will no doubt be explained some day, that a product with an active polarity has never under any circumstances been obtained by starting from an inactive substance, although nearly all the substances elaborated by nature in the vegetable organism are dissymmetric in the same manner as tartaric acid. What gives to this fact of the transformation of dextro-tartaric acid a particular originality is, that I have ascertained that in the same circumstances lævo-tartaric acid also becomes converted into racemic acid. What a strange tendency is exhibited by these natural organic bodies! a totality of dissymmetric dextro- or lævo-molecules becoming half transformed, simply by the influence of an elevated temperature, into inverse molecules, which, when once produced, combine with the first.

During a long period I had regarded the production of racemic acid from tartaric acid as impossible. In fact, I supposed that racemic acid was a combination of lævo-tartaric acid with dextro-tartaric acid. The conversion of dextro-tartaric acid into racemic acid is consequently of the same nature as that of the transformation of dextro-tartaric acid into lævo-tartaric acid. Now all that can be done with the dextro-tartaric acid can be effected under the same circumstances with the lævo-tartaric acid. If, therefore, any operation performed with the dextro-acid changed its direction of rotation to the left, the same operation performed with the lævo-tartaric acid would render it right. The transformation therefore appears impossible; at the most we may arrive at an inactive acid.

Fortunately experiment has contradicted these theoretical deductions. However, they served me as guides; and the less I was disposed to seek for the conversion of tartaric acid into racemic acid, the more I endeavoured to produce inactive tartaric acid. Not only did the existence of this acid appear to me to be theoretically possible, but I also knew the intimate connexion between tartaric and malic acids, and I had already obtained inactive malic acid. Now it is in seeking for inactive tartaric acid that I ascertained the convertibility of tartaric acid into racemic acid. But the same operation, fortunately and singularly, furnished me also with considerable quantities of inactive tartaric acid. In other words, I have obtained, together with racemic acid, a tartaric acid which has no action upon polarized light, and which is moreover capable of being resolved, under the same circumstances as racemic acid, into dextro- and lævo-tartaric acids; an extremely curious acid, crystallizing readily, and giving salts which yield neither to the

tartrates nor to the racemates in beauty of form. I have already said, that after treating tartrate of cinchonine, which had been exposed for several hours to a heat of 338° F., with water, and adding chloride of calcium to the liquid, the racemic acid formed at the expense of the tartaric acid is precipitated in the form of racemate of lime. If the liquid be immediately filtered to separate the racemate, a fresh crystallization is deposited in about twenty-four hours; this consists of pure inactive tartrate of lime, from which the inactive tartaric acid may be readily extracted.

Lastly, I have ascertained that the inactive tartaric acid is produced in the preceding operation entirely at the expense of the racemic acid already formed. This is proved by the fact, that if racemate of cinchonine be kept at a temperature of 338° F. for several hours, a considerable portion of it is converted into this inactive tartaric acid.

We consequently now know four tartaric acids,—dextro-tartaric acid; lævo-tartaric acid; the combination of both, or racemic acid; and the inactive acid, which deviates neither to the right nor left, nor is formed by the combination of the dextro- and lævo-tartaric acids. There is no doubt that this series of four isomeric tartaric acids is a type round which a multitude of others will range hereafter.

There is however a serious difficulty to be found in the ulterior applications of these new results. Thus to pass from dextro-tartaric acid to lævo-tartaric acid, it is necessary to pass through the racemic acid, which is a combination of the two, and then to split this combination. For this purpose I proposed the formation of the double salt of soda and ammonia. The crystals produced are of two sorts; these I separated by hand according to the character of their hemihedric form. This splitting is here accidental. It is no doubt a very curious phænomenon, for which however we see no proximate cause; besides, it is only one racemate that presents this faculty of splitting; consequently a new racemic acid might be obtained in some other series than the tartaric series, which probably it might be found impossible to resolve, and the inverse of the product started from to obtain it would remain unknown. This was until lately the state of the question; but I have recently found a chemical process, resting on general principles, for the resolution of racemic acid.

In a former memoir, I showed that the absolute identity of the physical and chemical properties of non-superposable right and left bodies ceased to exist when these products were placed in the presence of active bodies. Thus the dextro- and lævo-tartrates of the same active organic alkali are quite distinct in crystalline form, solubility, &c. It was to be hoped, therefore, that we might profit by this dissimilarity to isolate the two acids composing racemic acid; and for this purpose, after many fruitless researches, I have found means to render the two bases quinicine and cinchonicine serviceable. When racemate of cinchonicine is prepared, and its solution brought to a certain state of concentration, it always hap-

pens that the first crystallization is principally formed of lævo-tartrate of cinchonicine, the dextro-tartrate remaining in the mother-liquor. A similar result is presented with quinicine, only that in this case the dextro-tartrate is the first deposited. When, therefore, it is supposed that an organic product possesses a binary constitution analogous to that of racemic acid, its resolution should be attempted by placing it in contact with an active product, which, by the necessarily dissimilar properties of the combinations which it is capable of forming with the components of the complex group, will render the separation of the latter possible.—*Comptes Rendus*, August 1, 1853, p. 162.

On the Combination of Water and Boracic Acid with Oxide of Iron. *By* H. Rose.

When solutions, prepared in the cold, of pure crystallized sulphate of iron and ammonia ($NH^4O, SO^3 + Fe^2O^3, 3SO^3 + 24HO$) and neutral borate of soda ($NaO\,BO^3$), the latter in excess, are mixed together, a voluminous pale brown precipitate is obtained; it sinks slowly and with difficulty, and when dried becomes dark brown. If it has not been washed with water, it consists essentially of a compound of borate of iron with neutral borate of soda; and when dried at 212° F., its composition may be expressed by the formula $4(Fe^2O^3\,BO^3, HO) + NaO, BO^3 + 2HO$. That it is really a chemical compound of borate of iron and neutral borate of soda, and not merely a mixture, appears from the fact, that during drying it does not attract carbonic acid from the air, like the neutral borate of soda, which cannot for that reason be dried and freed from its water of crystallization without becoming changed partly into carbonate and partly into biborate of soda.

This compound however is of so weak a nature that it may be destroyed by mere washing with cold water. After the voluminous precipitate had been washed with cold water, its colour became darker; it then contained no soda, but had also lost considerably in boracic acid. After drying at 212° F., its composition might be expressed by the formula $Fe^2O^3, BO^3\,HO + 5(Fe^2O^3, HO)$.—The water had thus not only removed the neutral borate of soda, but also five-sixths of the boracic acid of the borate of iron, the latter being replaced by water.

If, instead of neutral borate of soda, a solution of the biborate be employed for the precipitation of the sulphate of iron and ammonia, a pale brown voluminous precipitate is also produced on mixing the cold solutions; this consists of borate of iron and biborate of soda. When dried at 212° F., its composition may be expressed by the formula $4(Fe^2O^3, BO^3 + HO) + NaO, 2BO^3 + 5HO$. This precipitate also loses the borate of soda, and the greater part of the boracic acid of the borate of iron, when washed with cold water. The precipitate, when washed and dried at 212° F., had the composition $Fe^2O^3, BO^3 + HO + 8HO\,Fe^2O^3$. Thus by washing with cold water, it had lost, besides the biborate of soda, still more boracic acid from

the borate of iron than the precipitate produced by neutral borate of soda.—*Monatsbericht der Akad. der Wiss. zu Berlin*, June 1853, p. 363.

On some Seleniates and Selenites of Mercury. *By* F. Köhler.

The author has investigated the ore of quicksilver, brought by the late C. Ehrenberg from Onofrio in Mexico, and prepared some selenic and selenious acid salts of the oxides of mercury.

Selenite of the Protoxide of Mercury, Hg^2O, SeO^2, which has already been described by Berzelius, was obtained by the author by the precipitation of protonitrate of mercury with selenite of soda. It forms a white powder, unchangeable by light, which undergoes no loss of weight either under the air-pump or in the water-bath. When more strongly heated, it gives off a very small quantity of water, becomes straw-yellow, and evolves a yellow smoke, whilst selenious acid and mercury are sublimed with partial decomposition of the salt; it fuses at last into a dark brown fluid, which when boiled volatilizes completely, and sublimes in the form of brown drops, which become transparent and of a pale amber or sulphur-yellow on cooling, and are amorphous when solid; this very characteristic behaviour was described by Berzelius.

It is not attacked by water; it is insoluble in cold, but perfectly soluble in hot nitric acid; muriatic acid renders it red from separation of selenium; solution of potash renders it black. Analysis:—

Hg^2O	79·498	1	78·917
SeO^2.....	20·341	1	21·083

The *anhydrous salt* was found by the author on the Mexican ores in the form of a straw- or citron-yellow powder. These ores appeared to be fragments of veins, in which corroded quartz runs through calc-spar, and through which the sulphoseleniuret of mercury analysed by H. Rose, a little cinnabar, much pure mercury, chloride of mercury, and selenite of the protoxide of mercury (*onofrite*) are scattered. An analysis of the mixture in which the onofrite occurs gave—

3·529 selenite of the protoxide of mercury.
56·987 protochloride of mercury.
31·225 metallic mercury.
4·390 calc-spar.
3·236 quartz.
Trace of silver.

Acid Selenite of Mercury, $3Hg^2O + 4SeO^2$, is produced from the neutral salt by fusing it at 356° F., and then heating it above its melting-point. It forms a dark vermilion-red, opake mass, with a radiate crystalline fracture, similar to the sulphuret of potash; its specific gravity is 7·350 at 56°·3 F. It exhibits the general behaviour of the neutral salt both in the humid and dry way, except that it is but little changed even by boiling nitric acid, and that when

heated it furnishes a still more abundant sublimate of selenious acid. Analysis—

Hg^2O	73·507	3	73·735
SeO^2	26·236	4	26·265

Seleniate of the Protoxide of Mercury, $6Hg^2O + 5SeO^3$.—This is produced by mixing a solution of seleniate of soda with protonitrate of mercury, and washing. A white precipitate is first thrown down, apparently a neutral salt, which only becomes yellow when washed, and then forms this salt. After drying in the water-bath, the salt has a slight yellowish colour, which soon changes to gray when exposed to the light. Solution of potash immediately renders it black; nitric acid, even when boiling, affects it but slightly, although its colour becomes white. Cold muriatic acid effects no change in its colour; when heated, it renders the salt red in consequence of the separation of selenium. Analysis—

Hg^2O	78·604	6	79·734
SeO^3	21·216	5	20·266

Selenite of the Peroxide of Mercury, $7HgO + 4SeO^2$, was obtained by boiling oxide of mercury, prepared in the humid way, with a watery solution of selenious acid. The oxide of mercury acquired a pale yellow colour, but was not dissolved. The pale yellow amorphous salt, which undergoes no change by exposure to light, dissolves with difficulty in hot nitric acid, but readily in muriatic acid; with potash, yellow oxide of mercury is separated; when heated, it furnishes a very small quantity of water, and a considerable quantity of sublimed selenium; it then fuses into a brown fluid, which sublimes in sulphur-yellow drops, leaving a small residue of oxide of mercury, which is gradually decomposed and volatilized only by an increase of heat. Analysis gave—

HgO	76·987	7	77·278
SeO^2	22·521	4	22·722

Basic Seleniate of Mercury, $2([HgO]^3, SeO^3) + HO$.—Oxide of mercury, prepared in the humid way, is boiled with a watery solution of selenic acid. The salt remains nearly undissolved, only a small portion being taken up. The salt which remains undissolved in the selenic acid has, whilst moist, a bright red colour, like that of basic chromate of lead; this, when dried in the air, and decomposed in the water-bath, becomes somewhat brownish, but then undergoes no further change. It is insoluble in cold nitric acid, but dissolves readily in this acid when heated; it is readily dissolved by muriatic acid, and gives yellow oxide of mercury when treated with potash. When heated, it first of all furnishes a small quantity of water without fusing, but with the acquisition of a blackish-brown colour; reduced mercury, selenious acid, and selenite of protoxide of mercury then make their appearance; the residue at length fuses, whilst sublimation of the substances just mentioned takes place; it again becomes solid when oxide of mer-

cury, which requires a stronger heat for its decomposition, alone remains. Analysis—

HgO	82·747	6	82·641
SeO^3	15·523	2	16·212
HO	1·205	1	1·147

Neutral Seleniate of Mercury, HgO SeO^3 + HO.—The acid fluid poured from the preceding salt, when evaporated at a very gentle heat, furnished a deposit of very small wart-like groups of a concentric fibrous structure, which were dried first on a porcelain plate, and afterwards under the air-pump. In this state the salt had the appearance of a collection of light dull grains of a dingy grayish-yellow colour, which changed no further on exposure to light. When water was poured over it, it rapidly acquired a red colour, and left a large quantity of the red basic salt, whilst only a small quantity was dissolved as an acid salt. Potash separates yellow oxide from it. When heated, it fuses very readily, and furnishes first water, then selenious acid, which forms large crystals with the water, reduced mercury, and yellow drops of selenite of protoxide of mercury, leaving as residue a small quantity of oxide. Analysis—

HgO	59·253	1	59·856
SeO^3	35·163	1	35·204
HO	4·043	1	4·980

Poggendorff's *Annalen*, lxxxix. p. 146.

On the Products of Decomposition of the Cyanic Æthers. *By* A. Wurtz.

When cyanic æther, $C^6 H^5 NO^2$, is brought into contact with water, carbonic acid is evolved, whilst *diæthylurea* is formed. This æther also acts, with but few exceptions, upon all the compounds derived from the type water; and the products of the reaction are to a certain extent similar to those just mentioned. Carbonic acid is often evolved, and a product referable to the *amides* is always formed. Diæthylurea certainly is not an amide, but it is most distinctly allied to the amides, being isomeric with diæthylcarbamide; and there is nothing against the supposition that it arises from the molecular transposition of the latter, as urea is formed from carbamide. The following formulæ show the relations existing between these products:—

$$\underbrace{C^2 O^2, N^2 H^4}_{\text{Carbamide.}} = \underbrace{N^2 \left\{ \begin{matrix} H^4 \\ C^2 O^2 \end{matrix} \right.}_{\text{Urea.}}$$

$$\underbrace{C^2 O^2, N^2 \left\{ \begin{matrix} H^2 \\ (C^4 H^5)^2 \end{matrix} \right.}_{\text{Diæthylcarbamide.}} = \underbrace{N^2 \left\{ \begin{matrix} H^2 \\ (C^4 H^5)^2 \\ C^2 O^2 \end{matrix} \right.}_{\text{Diæthylurea.}}$$

When cyanic æther is mixed with monohydrated acetic acid, $\left.\begin{matrix} C^4 H^3 O^2 \\ H \end{matrix}\right\}$, carbonic acid is disengaged and *æthylacetamide* is formed. This reaction is expressed by the following formula:—

$$\underbrace{\left.\begin{matrix} C^4 H^3 O^2 \\ H \end{matrix}\right\} O^2}_{\text{Acetic acid.}} + \underbrace{C^6 H^5 NO^2}_{\text{Cyanic æther.}} = C^2 O^4 + \underbrace{N\left\{\begin{matrix} C^4 H^5 \\ C^4 H^3 O^2 \\ H \end{matrix}\right.}_{\text{Æthylacetamide.}}$$

When about equal volumes of cyanic æther and anhydrous acetic acid are enclosed in a green glass tube hermetically sealed, a reaction is produced if the tube be immersed in an oil-bath heated to about 356° F. Carbonic acid and æthyldiacetamide, $N\left\{\begin{matrix} C^4 H^5 \\ C^4 H^3 O^2, \\ C^4 H^3 O^2, \end{matrix}\right.$ are formed, as shown by the following equation:—

$$\underbrace{\left.\begin{matrix} C^4 H^3 O^2 \\ C^4 H^3 O^2 \end{matrix}\right\} O^2}_{\text{Anhydrous acetic acid.}} + \underbrace{C^6 H^5 NO^2}_{\text{Cyanic æther.}} = \underbrace{N\left\{\begin{matrix} C^4 H^5 \\ C^4 H^3 O^2 \\ C^4 H^3 O^2 \end{matrix}\right.}_{\text{Æthyldiacetamide.}} + C^2 O^4$$

Æthylacetamide and æthyldiacetamide are evidently analogous to the compound amides recently obtained by M. Gerhardt by a totally different process.

Alcohol itself may be referred to the type water. Cyanic æther splits it like the preceding compounds, except that no carbonic acid is disengaged in the reaction; the elements of the two substances combine to form a new amide, *æthylurethane*. This reaction is explained by the following equation:—

$$\underbrace{\left.\begin{matrix} C^4 H^5 \\ H \end{matrix}\right\} O^2}_{\text{Alcohol.}} + \underbrace{C^6 H^5 NO^2}_{\text{Cyanic æther.}} = \underbrace{C^{10} H^{11} NO^4}_{\text{Æthylurethane.}}$$

Æthylurethane may be regarded as æthylcarbamic æther, and is consequently connected with the amides, like carbamic acid itself.

Common æther, $\left.\begin{matrix} C^4 H^5 \\ C^4 H^5 \end{matrix}\right\} O^2$, does not act, or acts with great difficulty, upon cyanic æther. The author enclosed these fluids in very strong tubes, and plunging these into oil-baths, submitted the mixture contained in them to very high temperatures and immense pressure. On opening them after cooling, no disengagement of gas was observed; the distillation of the contents restored the æther and cyanic æther unchanged, except that at the close of the operation a very small quantity of a fluid, which the author supposes to be *diæthyluræthane*, was obtained.

The author explains the difficulty with which ordinary æther acts upon cyanic æther in the following manner:—If ordinary æther be

water, H^2O^2, in which the molecules of hydrogen are replaced by 2 molecules of the æthyle group (C^4H^5), the introduction into the water type of these 2 voluminous molecules may tend to render the combination stable, and the reactions less easy in consequence.

The author proposes to investigate the action of cyanic æther upon the compound æthers, such as acetic æther. In this case *diæthylacetamide* may probably be formed in the following manner:—

$$\left.\begin{matrix} C^4H^3O^2 \\ C^4H^5 \end{matrix}\right\} O^2 + C^6H^5NO^2 = C^2O^4 + N\left\{\begin{matrix} C^4H^5 \\ C^4H^5 \\ C^4H^3O^2 \end{matrix}\right.$$

Acetic æther. Diæthylacetamide.

Comptes Rendus, August 1, 1853, p. 180.

Analysis of Rain-Water. By M. Martin.

The author examined about 14 litres of the water which fell at Marseilles during a violent storm on the 27th of May of the present year.

He did not find the least indication of the presence of iodine in the water.

The determination of the chlorine, made by the volumetric method, gave 0·00429 grm. of chlorine, corresponding to 0·00706 grm. of chloride of sodium, a quantity far greater than has hitherto been found.

The determination of the ammonia was effected by M. Boussingault's method; it gave 0·003144 grm. for the kilogrm. of water.

No traces of nitric acid were discovered.—*Comptes Rendus*, Sept. 26, 1853, p. 487.

On the Presence of Methylamine in the Products accompanying Acetone. By C. Greville Williams*.

Hoffman's discovery of trimethylamine in herring-brine, Anderson's researches on bone-oil and codeine, and Rochleder's experiments on caffeine, show us that the volatile bases of Wurtz, and several others, are frequently formed under unexpected circumstances, and render it highly probable that one or more of these remarkable substances generally accompanies the ammonia in the destructive distillation of nitrogenous animal and vegetable matters.

Having occasion, while preparing acetone, to distil some hundredweights of crude acetate of lime, the impure product was placed in a water-bath connected with a condensing apparatus, and the acetone, still contaminated with water and oily matters, was rectified *per se* at about 200°.

The residue of the operation, consisting of tarry substances and the chief part of the water, had a strong alkaline reaction, and gave copious fumes on the approach of a rod dipped in hydrochloric acid.

* Communicated by the Author.

It had a singular pungent odour, adhering strongly to the clothes, and after exposure to the air, becoming in some degree like fish. As it was therefore suspected that some of Wurtz's bases might be present, the liquid was treated with excess of lime, and the distillation repeated. The liquid now obtained was freed by a separator from the greater part of the tar and oils, saturated by sulphuric acid, and evaporated to dryness; on resolution in water and filtration, some impurities were got rid of, and the brown filtrate was treated with potash in an apparatus connected with some Woulfe's bottles containing hydrochloric acid.

The acid in the first bottle rapidly acquired a reddish-brown tint, and became nearly saturated.

This process was repeated, with the difference, that excess of lime was used instead of potash, and no heat was applied until the evolution of an absorbable gas had nearly ceased, and then the temperature used was as low as possible to prevent the tarry matters from coming over.

The still slightly coloured liquid was evaporated to dryness on the water-bath, and digested in a small quantity of boiling absolute alcohol, and the liquid filtered when nearly cold. In this manner a large quantity of chloride of ammonium remained on the filter.

The alcoholic solution, evaporated to dryness, gave a small quantity of a slightly coloured salt.

The sal-ammoniac was converted into platinum salt, and burned, to ascertain its freedom from the other base.

I. 16·300 grs. platinum salt gave 7·815 platinum.
II. 13·900 grs. platinum salt gave 6·630 platinum.

	I.	II.	Mean.	Theory.
Or, per cent.....	47·94	47·69	47·81	47·72

The first and second experiments were made with salts obtained from different samples of acetate of lime.

The alkaline chloride obtained from the alcoholic solution was so small in quantity, that it was not thought desirable to sacrifice any portion in the endeavour to get it absolutely free from colour; it was therefore at once converted into platinum salt, which, after well washing with alcohol, was dissolved in a little boiling water, and filtered from a trace of insoluble matter.

On cooling, the solution deposited a quantity of beautiful golden-yellow crystals, amounting to 3·695 grs., which on being burnt left 1·565 platinum. (I.)

The mother-liquor of the crystals, evaporated to dryness, gave 2·115 of the salt, which on burning gave 0·875 platinum. (II.)

On reducing these numbers to per-centages, we obtain a close approximation to the quantity of platinum in the platino-chloride of methylamine:—

I.	II.	Mean.	Theory.
42·35	41·37	41·86	41·61

The production of methylamine in the destructive distillation of one of the substances obtained in the manufacture of methylic alco-

hol, would, even in the absence of Hoffman's experiments on the decomposition of the æthylic and methylic iodides by ammonia, be strong corroborative evidence of the correctness of the derivation which has been assigned to it.

Laboratory, Oxford Court,
October 5, 1853.

ANALYTICAL CHEMISTRY.

On the Analysis of Cast Iron.

By Professors CAMPBELL MORFIT *and* JAMES C. BOOTH.

[Extract from the Official Report to Captain L. A. B. Walbach, U.S. Ordnance, on Foundry Service, upon the Examination of Gun Metal.]

[Concluded from page 398.]

Tin and Titanium.

THE filter *a*, which was set away in the early stages of the process, contained all the silex and slag, tin and titanium, with some carbon. The slag, silex, and carbon having been determined in previous essays, it was reserved for the estimation of the two remaining components. A qualitative examination is only necessary generally, for in no one of our samples did we find even traces. Still they may occasionally exist, and must be sought, and if largely present, separated in the usual manner.

Tin.—If tin existed in the metal, it was converted into insoluble stannic acid by the oxidizing action of the nitric acid and subsequent evaporation, and remained with the insoluble residue. Its presence is proved by fusing the suspected insoluble residue on charcoal with carbonate of soda, grinding that part of the coal in an agate mortar with water, and washing over with water until all the charcoal and other light particles have been removed, when tin will betray itself by silvery spangles and streaks produced by the pestle.

Titanium.—The presence of titanium is best shown by fusing the whole residue with carbonate of soda, extracting with lukewarm water, filtering, partially neutralizing, and boiling; titanic acid will precipitate. A yellowish tint in the soda solution will also indicate the presence of chrome.

Arsenic, Antimony and Sulphur.

As these components, if present, exist in quantities too minute to be estimated from 1 grm. of metal, a new portion of 5 grms. of *clippings* must be treated specially for the purpose.

Arsenic.—These are placed in a beaker of 16 oz. capacity, and drenched with a fluid ounce of pure nitric acid. The glass is covered with an inverted capsule, and very gradually heated to boiling by a small spirit-lamp. As the digestion progresses, 13 to 15 grms. of finely-powdered chlorate of potash are added portionwise, and the heat continued until the insoluble particles become flotant, when

the digestion is completed. The nitric acid and chlorate of potash, having eminent oxidizing powers, convert most of the ingredients wholly into a soluble form. The metals being oxidized, their oxides dissolve in the acid; the sulphur and arsenic have become soluble arseniate and sulphate of potash; and carbon, silex, and slag remain as insoluble residue. The liquor is evaporated to dryness to render silica insoluble, redigested in hydrochloric acid to remove oxide of iron, &c., diluted with water, filtered and hot-washed. The filter is rejected, its contents having been already estimated in previous essays. The filtrate is G.

Aqua regia cannot be substituted for the mixture of nitric acid and chlorate of potash, for the amounts of sulphur and arsenic are so small that portions may be volatilized as gaseous hydrogen compounds. Nitric acid alone is slow in action, and the addition of *fuming* nitric acid to hasten its action might introduce the very substances it is desired to detect, for that reagent is seldom pure.

If the size and distinctness of the tache formed upon the porcelain in the qualitative essay indicated an appreciable quantity of arsenic, the process must be continued as follows, to separate and estimate it quantitatively.

The filtrate G contains all the ingredients in a soluble form, except those separated by the filter; but owing to a large excess of potash salt, which is difficultly removed, is valuable only for the sulphur and arsenic.

It is difficult to estimate arsenic quantitatively by that modification of Marsh's process, by which the arseniuretted hydrogen is reduced by heating the middle of the exit-tube, for a portion of it may escape decomposition, and the black ring of arsenic obtained in the tube beyond the heated part will only represent a fraction of it. It is true, that Lassaigne's improvement, to conduct the excess of gas into a solution of nitrate of silver, recovers the whole of the arsenic; but we believe that a modification of Reinsch's is a more effectual plan.

Strips of bright copper are introduced into the heated filtrate G, until a fresh surface ceases to be tarnished. The strips are then removed, rinsed in distilled water, and, when dried, carefully laid upon a sheet of glazed paper, and the tarnished coating entirely scraped off with a knife. The scrapings, carefully collected, are introduced into a long and narrow glass tube, and heated to sublime the arsenic as arsenious acid. The upper part of the tube, containing the sublimate, is then cut off, and with its contents accurately weighed. The arsenious acid having been removed by hydrochloric acid and water, the empty tube is dried, and again weighed. The difference in weight expresses the amount of arsenious acid in the filtrate, whence the metallic arsenic is calculated. A more critically-accurate method would be to dissolve the scrapings in nitromuriatic acid, and to estimate the arsenic acid from the filtered solution by a given weight of metallic iron, as directed for phosphorus.

Antimony.—The only two substances in cast iron precipitated by

the metallic copper are arsenic and antimony; and as the two are frequently associated, and give similar metallic stains, we thought it advisable in estimating one to test for the presence of the other. This was done by adding to the tache, on the china, a concentrated solution of iodate of potash, which, according to Slater (Chem. Gaz., ix. 57), reddens, and immediately dissolves arsenical stains, while upon those of antimony it exerts no visible action for several hours. Chlorinated soda or lime will also instantly dissolve arsenic, and leave the antimony.

Sulphur.—If the tache do not indicate an appreciable quantity of arsenic, the preceding manipulations may be omitted; otherwise, after it has been separated, as above directed, chloride of barium is poured into the residual liquor, the whole stirred, and left to repose for several days. If the content of sulphur is very minute, cloudiness does not manifest itself for several hours; and in such cases a week's repose is necessary to ensure the entire subsidence. It must then be filtered off, washed with diluted hydrochloric acid and hot water, ignited, weighed, and the amount of sulphur calculated from the weight of sulphate of baryta.

It is proper to observe, in order to provide against the possibility of error, that some caution is necessary as to the nature of the precipitate; for if the solution be concentrated, a portion of the chloride of barium, which is generally added in excess, may ultimately fall in fine crystalline powder, but it will disappear during washing on the filter. The previous acidulation of the liquid prevents the precipitation of carbonate, phosphate, or arseniate of baryta.

Nitrogen, Oxygen and Aridium.

Nitrogen.—The doubts of many of the best chemists as to the presence of this element in cast iron, having been confirmed by the recent experiments of a careful investigator, we omitted searching for it.

Oxygen.—We doubt the presence of oxygen as an essential ingredient of recently made metal, except in the minute portions of slag accidentally remaining in it, and which sometimes contains a silicate of the oxide of iron.

Aridium.—Aridium, said to have been found in some Swedish ores, was not observed by us in our examination.

On the Separation of Manganese from Iron and Nickel. *By* Dr. T. Schiel.

A stream of chlorine, passed through a solution of protochloride of manganese to which acetate of soda has been added, produces a precipitate of peroxide of manganese. Iron and nickel are not precipitated; cobalt is separated as oxide.—Silliman's *American Journal*, xv. p. 275.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Hull, September 7th, 1853.

On the Employment of Pentasulphide of Calcium as a Means of preventing and destroying the Oïdium Tuckeri, *or Grape Disease.* *By* Astley Paston Price, Ph.D., F.C.S., *Chemical Assistant in the Laboratory of the Government School of Mines.*

Of those substances which have been employed to arrest the devastating effects of this disease, none appear to have been so pre-eminently successful as sulphur, whether employed as powdered or flowers of sulphur, or by sublimation in houses so affected. But notwithstanding the several methods described for its application to the vines, I am not aware that any has, or had, appeared prior to 1851, when these experiments were instituted, by which sulphur might be uniformly distributed over, and become to a certain extent firmly attached to the vines.

Three houses, situated at Margate in Kent, in the vicinity of the one in which the disease first made its appearance in England, having been for five consecutive years infected with the disease, and notwithstanding the employment of sulphur as flowers of sulphur, no abatement in its ravages could be detected, I was induced to employ a solution of pentasulphide of calcium, a diluted solution of which having been found to act in no way injuriously to the young and delicate shoots of several plants, was applied to the vines; the object in view being that the pentasulphide should be decomposed by carbonic acid, and that 4 atoms of sulphur, together with the carbonate of lime formed, should be deposited in a uniform and durable covering on the stems and branches of the vines affected. Although but few applications were made, the stems became coated with a protective deposit of sulphur, and the disease gradually but effectively disappeared, insomuch that the houses have been, and now are, entirely free from any disease or symptoms of infection.

The young shoots are in no way affected by its application, and the older wood, covered with the deposited sulphur, continues exceedingly healthy.

The specimens exhibited to illustrate the durability and protective influence of the deposited sulphur were from vines which in the autumn of 1851 were covered with the disease, but which since the autumn of 1852 have received no further treatment.

The vines in the immediate neighbourhood, and adjoining one of the houses, are covered with the disease; but notwithstanding their close proximity, no indication of the disease has at present been detected in either of the three houses.

A solution of pentasulphide of calcium is prepared by boiling 30 parts by weight of caustic lime with 80 parts by weight of flowers of sulphur, suspended in a sufficient quantity of water; heat is ap-

plied until the solution has acquired a dark red colour, and the excess of sulphur ceases to dissolve. The clear solution is drawn off, and after dilution with water may be applied to the vines by means of either a sponge, brush or syringe. A saturated solution of pentasulphide of calcium may be diluted with from 12 to 20 times its volume of water previous to being employed.—*Communicated by the Author.*

On the Chemical Action of the Solar Radiations.
By Mr. R. Hunt.

This was a report to the Section of the continuation of an examination of the chemical action of the rays of the prismatic spectrum, after it had been subjected to the absorptive influences of different coloured media. The mode of examination adopted has been to obtain well-defined spectra of a beam of light passing through a fine vertical slit in a steel plate by prisms of flint and crown glass, and of quartz. The spectrum, being concentrated by a lens, was received upon a white tablet, and submitted to careful admeasurement; the coloured screen (sometimes coloured glass, and sometimes coloured fluid) was then interposed, and the alterations in the chromatic image were carefully noted; the chemical preparation was then placed upon the tablet, and the chemical impression obtained. The relation which this image bore to the luminous image was a true representation of the connexion between the colour of a ray and its power to produce chemical change. In the report made to the Belfast Meeting of the British Association, the results of experiments made upon glass tablets prepared by the so-called collodion process were alone given. In the present report the examination has been extended to the photographic preparation known as the calotype, and to iodide and bromide of silver in their pure states and when excited by gallic acid. M. Edmond Becquerel, in a paper communicated to the Academy of Sciences, of which an abstract appears in the 'Comptes Rendus,' vol. xvii. p. 883, states "that when any part of the luminous spectrum is absorbed or destroyed by any substance whatever, the part of the chemical rays of the same refrangibility is equally destroyed." The author's experiments, as recorded in the former report, and those now detailed, prove that this conclusion has been formed too hastily. Although there are many absorptive media which, at the same time as they obliterate a particular coloured ray, destroy the chemical action of that portion of the spectrum, yet there are a still more extensive series which prevent the passage of a ray of given refrangibility, and do not, at the same time, obstruct those rays which are chemically active of the same degree of refrangibility. This is particularly exemplified in the case of glasses coloured yellow by different preparations. With some of these the blue rays are obliterated, the chemical action of this part of the spectrum not being interrupted; whereas in some other examples those rays permeate the glass, but are

almost entirely deprived of chemical power. A still more curious fact is noticed in this report, for the first time, of some media which have the power, as it were, of developing chemical action in a particular part of the spectrum where the rays did not appear previously to possess this power. Several glasses exhibited this phænomenon to a certain extent, particularly such as were stained yellow by the oxide of silver; but one glass showed this in a remarkable manner. This glass was yellow when viewed by transmitted light, but it reflected pale blue light from one of its surfaces; it obliterated the more refrangible rays down to the green, and rendered the yellow rays far less luminous than usual. In nearly every case the yellow rays are found to be not merely inactive, chemically, but to prevent actively chemical action. After the spectrum has been submitted to the action of this glass, *all chemical power is confined to this yellow ray.* The author has hitherto supported the view, that photographic phænomena and the illuminating power of the sunbeam were distinct principles, united only in their modes of motion. He was led to this from observing that where there was the most light there was the least power of producing chemical change; and that as illuminating power diminished, the chemical phænomena of the solar rays increased. The results, however, which he has obtained during the brief sunshine of the present summer, lead him to hold that opinion in suspension. In many of the spectra obtained (copies of which will be appended to the printed report) there appears to be evidence of the conversion of one form of force into another, the change indeed of *light* into *actinism* or chemical power; and, again, as in Mr. Stokes's experiments, the exhibition of the ordinarily invisible chemical rays in the form of *light.—Athenæum.*

On a new Method for determining the Commercial Value of Oxide of Manganese. By Astley Paston Price, Ph.D., F.C.S., *Chemical Assistant in the Laboratory of the Government School of Mines.*

It is well known that several methods have been described for determining the commercial value of oxide of manganese, that is to say for estimating the amount of chlorine capable of being obtained from a given sample of manganese.

There are, however, certain practical inconveniences attendant on the employment of many of these processes, most of them demanding an amount of time and manipulation which it is most desirable to obviate.

The method I have for some time employed, and which I have found to give accurate results, is based on the conversion of arsenious into arsenic acid by means of chlorine, and the transformation of arsenious into arsenic acid by the employment of a solution of hypermanganate of potash.

The specimen of manganese under examination is dissolved in a normal hydrochloric acid solution of arsenious acid; and the

arsenious acid remaining unchanged into arsenic acid is determined by a standard solution of hypermanganate of potash. In employing a solvent containing a reducing agent, it will be found that the solution of the oxides of manganese is materially facilitated, and may be effected at a low temperature in a very short space of time.

In adopting this method, some difficulties presented themselves:—

1. On dissolving arsenious acid in hydrochloric acid, terchloride of arsenic is given off, and it becomes difficult to obtain a correct normal solution. This difficulty is avoided by dissolving the arsenious acid in a solution of caustic potash, and then adding the alkaline solution to an excess of hydrochloric acid.

Another difficulty occurred in effecting the solution of the oxide of manganese in the arsenical solution, as in proportion to the elevation of temperature does the loss of terchloride of arsenic increase. This source of error is prevented by employing a dilute acid solution of arsenious acid, and adapting one of Will's nitrogen bulbs, containing a solution of potash, to the flask in which the oxide of manganese is dissolved. Any terchloride of arsenic which may pass over is there effectually retained, provided solution be effected at a low temperature. The normal solution of arsenious acid is made by dissolving 113·53 grs. of arsenious acid, corresponding to 100 grs. of peroxide of manganese, in a solution of potash, and then adding hydrochloric acid until the solution occupies 100 measures.

A standard solution of hypermanganate of potash is obtained by diluting, for example, 5 measures of the normal solution of arsenious acid, corresponding to 5 grs. of peroxide of manganese, and then determining the number of measures of the solution of hypermanganate of potash that are required to transform the arsenious acid therein contained into arsenic acid.

These two solutions being obtained, an estimation of the value of a specimen of oxide of manganese may be expeditiously and accurately made.

Ten, or any number of grains of the specimen under examination, are placed in a small flask, to which 10 or more measures of the normal arsenical solution are added, and to the flask is adapted one of Will's nitrogen apparatus, containing a solution of potash. The flask is then placed in a water-bath, or a gentle heat is applied until solution is effected. The contents of the flask, after having been allowed to cool, are, together with the solution of potash, transferred to a larger flask, and diluted with water. The amount of arsenious acid remaining unchanged is then determined by the addition of the standard solution of hypermanganate of potash, and the quantity thus indicated being deducted from the number of grains of arsenious acid employed in the first instance, will give the value of the specimen submitted to analysis.

In order to obtain correct results by this method, it is of course necessary that the hydrochloric acid and the potash employed should be free from sulphurous or nitric acid, or any other reducing or oxidizing impurities.—*Communicated by the Author.*

On the Origin and Composition of a Mineral called Rotten-Stone. By Prof. JOHNSTON.

After having stated the district, the Great Fin, Derbyshire, in which the mineral was found, the Professor went on to describe its chemical character and affinity. He observed that its component parts were not of a constant character, as had been asserted in some mineralogical works. Its origin was stated by Phillips to be from the decomposition of the slate rocks of Derbyshire. When examined under the microscope, it did not exhibit any organisms; but there were particles or bundles of some substance resembling the bituminous substances found near Castleford. Rotten-stone was found in lumps of all shapes and sizes, at depths varying from 2 to 6 feet below the surface of the earth. It was his (the Professor's) opinion that the rotten-stone was not the result of the decomposition of the shale of Derbyshire, but of the veins of black marble of the country, which had undergone a great change. In proof of this assertion, he produced specimens which he found to be black marble, with the merest coating of rotten-stone on them, whilst others were half rotten-stone and half black marble. The decomposition had been effected by dissolving the lime out of the rock, and not the rotting of the strata. This substance can be produced by dissolving the lime out of limestone, by bringing weak acids to bear upon it. This proved that there must necessarily exist in the soil some acid which dissolves the lime with which it comes in contact. Farmers would, therefore, see the necessity of adding lime to their land from time to time, because the lime kept continually washing away by the waters of heaven falling on it, and extracting from the rotting roots of the earth an acid which had a powerful effect not only on lime but on other mineralogical structures as well. —*Athenæum.*

On Crystals from the Sea-Coast of Africa. By J. PEARSALL.

The crystals here shown were obtained by Captain Mitchell, of the merchant ship 'Frankfield,' while searching the coast of Africa, between Saldanha Bay and the island of Ichaboe, for guano deposits. The crystals are of carbonate of lime, enclosing sand; 15 to 20 per cent. of sand is obtained from some specimens. The crystals are very hard, and have sharp cutting edges, so as to make it a painful task to walk upon them. The beach was covered with crystals to the extent of miles; about three miles was walked over, but it seemed as far as the eye could reach, and was one-half to one mile in breadth. Some of the specimens are from 4 to 5 inches in length, and with surfaces showing a thickness of $\frac{1}{2}$ an inch, and from 2 to 3 inches across the plane. The report given was that some of the crystals protruded up from the sands so far as to wound the ankles and legs without great care in walking over. Some crystals seem to be opake, with the sand enclosed except at the edges; 15 to 20 per cent. of sand is obtained from portions of crystals. Carbonate

of lime and magnesia, with small quantities of saline matter, common salt principally, can be obtained by breaking them up in distilled water. They are entirely soluble in diluted nitric acid. Mineralogists and chemists are perfectly well aware of the stony substance called Fontainebleau sandstone, where the sandstone is found having forms of crystals of carbonate of lime. The crystals now exhibited show the grains of sand of the beach enclosed, without altering the general form, and also that the crystal has at its base adapted itself to the sand and other crystals.—*Athenæum.*

Report on the Gases evolved in Steeping Flax, and on the Composition and Œconomy of the Flax Plant. By Prof. HODGES.

The gases of the fermenting vat have been analysed by the methods of Prof. Bunsen, and have been found to consist of carbonic acid, hydrogen and nitrogen. No sulphuretted hydrogen has, in any case, been detected. Several analyses of the proximate constituents of the dressed fibre and of its inorganic ingredients have been made, which show that a considerable amount of the nitrogenized and other constituents of the plant are retained in the fibre even after steeping and dressing have removed the structures unsuitable for textile purposes.—*Ibid.*

On a new Method for determining the Amount of available Chlorine contained in Hypochlorites of Lime, Soda or Potash. By ASTLEY P. PRICE, Ph.D., F.C.S., *Chemical Assistant in the Laboratory of the Government School of Mines.*

Numerous as have been the methods proposed for determining the available amount of chlorine in bleaching powder and other hypochlorites, there is not one that I am acquainted with by which correct and expeditious determinations can be made. The following method is based on the known reactions of hypochlorites of lime, potash or soda, and hypermanganate of potash, on arsenious acid, the former of which reactions has, as is well known, been frequently proposed as the principle of many ingenious chlorimetric processes. The application of hypermanganate of potash in the estimation of iron and other substances having been attended with such good practical results, I am led to anticipate that the extension of its application to the estimation of chlorine, in the manner hereafter described, may tend to simplify the manipulations, and curtail the time now requisite for determining the commercial value of the hypochlorites in the several conditions in which they are met with and employed in the arts. The first point to be attained, in the correct estimation of bleaching powder, is to effect complete solution without endangering a loss of available chlorine. This may be effected by weighing a given quantity of the specimen under examination into a large flask, and adding a normal solution of arsenite of potash or soda in such quantity that an excess be always present, and after dilution with water, gradually pouring in during agitation an excess of hy-

drochloric acid. A normal solution of arsenious acid is obtained by dissolving 139·63 grs. of arsenious acid, corresponding to 100 grs. of chlorine, in a solution of potash or soda, and diluting the solution with water to 1000 measures. If 50 measures of this normal solution be measured into a flask, and after dilution with water be acidified with hydrochloric acid, and to it be carefully added from a graduated burette a solution of hypermanganate of potash until the solution acquires a decided pink colour, the value of the solution of hypermanganate of potash will be obtained, as the number of measures employed will correspond to 5 grs. of chlorine. Having obtained a normal solution of arsenious acid and a standard solution of hypermanganate of potash, the commercial value of the hypochlorites of lime, potash or soda may be most easily determined. 100 grs. of the bleaching powder under examination are placed in a flask graduated to 1000 measures; 500 measures of the normal solution of arsenious acid are then added, and after dilution with water hydrochloric acid is gradually poured in until a slight excess has been employed. The solution is then made up to 1000 measures. If 100 measures of this solution be now transferred into a large flask diluted with water, and to it be gradually added from a burette a standard solution of hypermanganate of potash until the solution assumes a distinct coloration, the number of measures employed will indicate the amount of arsenious acid remaining unchanged into arsenic acid, which quantity being deducted from the amount of arsenious acid originally employed will give the proportion of available chlorine contained in the sample of bleaching powder. Thus supposing that 10 grs. of bleaching powder had been employed, and that 50 measures of the normal solution of arsenious acid, corresponding to 5 grs. of chlorine, had been added, and that 30 measures of the standard solution of hypermanganate of potash, corresponding to 3 grs. of chlorine, had been necessary to transform the excess of arsenious into arsenic acid, then the 10 grs. of bleaching powder would have contained 2 grs. of chlorine, or the value of the specimen would be 20 per cent.

Instead of employing 100 grs. of bleaching powder, and proceeding as before mentioned, any number of grains may be taken,—30 grs. I have found to be a very convenient quantity,—which being placed in a flask, a known quantity of the normal solution of arsenious acid is added, and after dilution with water, a clear solution is obtained by the addition of hydrochloric acid. To this a standard solution of hypermanganate of potash is added, and from the number of measures employed the value of the sample under examination is determined. With a small amount of practice, the estimations may be made in a very expeditious manner, and the results obtained I have hitherto found to be most satisfactory.

In the estimation of the commercial value of the hypochlorites of potash or soda, the amount of available chlorine will be indicated in the same manner, and with the same degree of accuracy as the determination of the value of bleaching powder.—*Communicated by the Author.*

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Combinations of Glycerine with Acids, and on the Synthesis of the Proximate Principles of the Animal Fats. *By* M. BERTHELOT.

THE author, after referring to the results obtained by his precursors in this department of chemistry, states that he has succeeded in combining glycerine with the true fatty acids, and also with other acids both organic and mineral. The substances thus produced are neutral and incapable of uniting with alkalies. Some are crystallized, others fluid.

They belong to several series of compounds. One series is identical with the natural neutral fatty bodies; another, and the most numerous, is analogous to the æthers. They may all be represented as acid + glycerine — water. Treated with alkalies, they all slowly reproduce the original acid and glycerine. Treated with concentrated muriatic acid, they are split up in the same manner; with alcohol and muriatic acid double decomposition takes place, furnishing glycerine and an æther of the acid previously united with the glycerine. Lastly, ammonia converts them into amides.

With the exception of three, which are volatile, they are decomposed by heat, furnishing acroleine. Yet stearine, oleine, margarine, and palmitine may be distilled in very small quantities *in vacuo* without furnishing acroleine or becoming acidified.

These substances are produced by the direct union of the acid and glycerine; this is effected by long contact in closed vessels with the aid of a more or less elevated temperature. Small quantities of most of them are formed even at ordinary temperatures. They are sometimes obtained by double decomposition between the æthers and glycerine. They are also produced by the action of muriatic acid on the mixture of glycerine and acid. This acid thus plays two opposite parts; dissolved in water and employed in large quantities, it causes the resolution of neutral fatty bodies into glycerine and fatty acids; when acting, in a gaseous state, upon a mixture of syrupous glycerine and an acid, it causes the combination of these two principles.

The author divides these substances into three groups—combinations of glycerine,—1st, with the fatty acids, reproducing the organic fatty substances; 2nd, with organic acids, forming sub-

stances not identical with any known organic bodies; 3rd, with mineral acids.

I. Combinations of Glycerine with the True Fatty Acids.

A. *With Fixed Fatty Acids.*

1. *Stearines.*—Stearic acid (fusible at 158° F., prepared according to M. Chevreul's method) forms three combinations with glycerine, —*monostearine*, *distearine* and *tetrastearine*, the latter identical with natural stearine.

Monostearine $\left\{\begin{array}{l} C^{42}H^{42}O^{8} = C^{36}H^{36}O^{4} + C^{6}H^{8}O^{6} - 2HO \\ C^{92}H^{163}O^{15} = C^{70}H^{139}O^{7} + 2C^{6}H^{16}O^{6} - 4H^{2}O \end{array}\right\}$

is obtained by heating equal parts of glycerine and stearic acid to a temperature of 392° F. for twenty-six hours. The glycerine and acid remain superposed, without any appearance of mutual solution. The neutral substance produced is also insoluble in glycerine. The solid stratum which floats upon the excess of glycerine is separated after cooling; it is then fused, some æther and slaked lime are added to it (the latter to separate any uncombined acid), and the whole kept at 212° F. for a quarter of an hour. The mass is then exhausted with boiling æther. The substance thus obtained is neutral, white, and very sparingly soluble in cold æther; it crystallizes in microscopic needles, which are usually grouped into rounded granules. It fuses at 142° F., and solidifies at 140° F. *In vacuo* it volatilizes without alteration. Heated in the air, it begins to evaporate, and then decomposes with formation of acroleine. It burns with a very luminous white flame.

Treated with oxide of lead at 212° F., it becomes saponified in a few hours, reproducing glycerine and stearic acid. The weight of the glycerine thus obtained is nearly one-fourth of that of the monostearine employed. When kept in contact for 106 hours with concentrated muriatic acid at 212° F., it resolves itself almost entirely into glycerine and stearic acid. Acetic acid mixed with alcohol does not decompose it under the same circumstances.

A similar compound is obtained by saturating the mixture of glycerine and acid at 212° F. with gaseous muriatic acid; but the compound thus obtained fuses at 116°·6 F., and is united with some chlorhydrine, from which it cannot be separated.

The mixture of glycerine and acid, when left standing for three months at the ordinary temperature, furnishes traces of a crystallized neutral fatty matter.

Distearine $\left\{\begin{array}{l} C^{78}H^{78}O^{12} = 2C^{36}H^{36}O^{4} + C^{6}H^{8}O^{6} - 2HO \\ C^{76}H^{151}O^{11} = C^{70}H^{139}O^{7} + C^{6}H^{16}O^{6} - 2H^{2}O \end{array}\right\}$

is obtained by keeping the mixture of equal parts of glycerine and stearic acid at a temperature of 212° F. for 114 hours. It is purified, like the preceding, by lime and æther. It is a neutral, white, granular substance, crystallizing in oblique doubly-refractive lamellæ. It fuses at 136° F., and solidifies at 131° F. When heated, it furnishes acroleine. Treated with oxide of lead at 212° F., it is resolved into glycerine and stearic acid. The same substance is obtained by heating the mixture of glycerine and acid to 527° F. for

seven hours; by heating 1 part of monostearine and 3 of stearic acid to 518° F.; or by exposing natural stearine with an excess of glycerine to a heat of 392° F. for twenty-two hours.

Tetrastearine $\left\{\begin{array}{l} C^{150}H^{146}O^{16}=4C^{36}H^{36}O^{4}+C^{6}H^{8}O^{6}-6H\,O \\ C^{146}H^{282}O^{14}=2C^{70}H^{139}O^{7}+C^{6}H^{16}O^{6}-6H^{2}O \end{array}\right\}$ is obtained by mixing monostearine with 15 or 20 times its weight of stearic acid, and heating it for several hours to 518° F. Water is eliminated, and condenses in the upper part of the tube. It is purified in the same manner as the preceding. It is neutral, and has the same composition as natural stearine.

2. *Margarines.*—Margaric acid (fusible at 140° F.) forms two combinations with glycerine,—*monomargarine* and *tetramargarine.*

Monomargarine ($C^{40}H^{40}O^{8}=C^{34}H^{34}O^{4}+C^{6}H^{8}O^{6}-2HO$) is formed either at 212° or at 392° F. It is even formed at ordinary temperatures, but in very small quantity. Its formation is easier than that of any other solid fatty matter. It fuses at 133°, and solidifies at 120° F. Treated with oxide of lead, it is resolved into glycerine and margaric acid. Its reactions resembled those of stearine, except that when heated for 106 hours to 212° F. with alcohol and acetic acid, it is partially decomposed, furnishing margaric æther and glycerine.

Tetramargarine appears to be formed by heating monomargarine to 518° F. with an excess of margaric acid. It has not been obtained quite pure. When saponified, it furnishes margaric acid and glycerine.

The stearic and margaric acids obtained by the saponification of the artificial stearines and margarines, are fusible respectively at 158° and 140° F.

3. *Palmitines.*—Palmitic acid forms three neutral combinations with glycerine; they are obtained under the same circumstances as the preceding.

Monopalmitine ($C^{38}H^{38}O^{8}=C^{32}H^{32}O^{4}+C^{6}H^{8}O^{6}-2HO$) fuses at 136°·4, and solidifies at 113° F.

Dipalmitine ($C^{70}H^{70}O^{12}=2C^{32}H^{32}O^{4}+C^{6}H^{8}O^{6}-2HO$) fuses at 138°·2, and solidifies at 133°·8 F.

Tetrapalmitine ($C^{134}H^{134}O^{16}=4C^{32}H^{32}O^{4}+C^{6}H^{8}O^{6}-6HO$) fuses at 140°, and solidifies at 114°·8 F. This is identical with natural palmitine.

Treated with oxide of lead, they all reproduce glycerine and palmitic acid, fusible at 141°·8 F. Monopalmitine, treated with alcohol and acetic acid at 212° F. for 102 hours, becomes decomposed, setting free glycerine. This property it shares with natural palmitine.

4. *Oleines.*—At 392° F., pure oleic acid forms a neutral *monoleine* ($C^{42}H^{40}O^{3}=C^{36}H^{34}O^{4}+C^{6}H^{8}O^{6}-2HO$). It is an oily liquid, which congeals about 59° F. Its spec. grav. is 0·947. Oxide of lead saponifies it very slowly and with difficulty. Alcohol and acetic acid do not decompose it at 212° F. In this respect it resembles natural oleine. It is also formed by double decomposition, when a mixture of oleic æther, glycerine, and muriatic acid are kept

at 212° F. The reaction commences even without the aid of the muriatic acid.

Dioleine ($C^{76}H^{74}O^{12}=2C^{36}H^{34}O^4+C^6H^8O^6-2HO$) is obtained by heating to 392° F., for twenty-two hours, a mixture of natural oleine and glycerine. Its spec. grav. is 0·921 at 70° F. It begins to crystallize about 59° F. It is also obtained by heating monoleine with oleic acid.

B. *With Volatile Fatty Acids.*

The volatile fatty acids also unite with glycerine, furnishing various liquid, neutral, odorous compounds. These are prepared by heating the mixture of acid and glycerine, saturating it, after cooling, with an excess of carbonate of potash, shaking with æther, evaporating on the water-bath, and drying by heat *in vacuo*. They are produced by leaving glycerine in contact with a volatile fatty acid for three months at the ordinary temperature, and also by the action of gaseous muriatic acid upon a mixture of glycerine and acid, or even of glycerine and the æther of a fatty acid.

They are resolved into acid and glycerine by alkalies, by solution of muriatic acid, and even by acetic acid or water. A mixture of alcohol and muriatic acid converts them into æthers and glycerine. Alcohol alone, employed in large quantities, is sufficient to induce this double decomposition, either by exposure to a temperature of 212° F. for eighty-eight hours, or with the assistance of the air, at ordinary temperatures.

1. *Valerines.*—The author has obtained two compounds:—

Monovalerine ($C^{16}H^{16}O^8=C^{10}H^{10}O^4+C^6H^8O^6-2HO$), formed at 392° F., is a neutral, oily, odorous fluid, of spec. grav. 1·100. It is slowly converted into valeramide by the action of ammonia.

Divalerine ($C^{26}H^{26}O^{12}=2C^{10}H^{10}O^4+C^6H^8O^6-2HO$) is a neutral oily fluid, of a disagreeable odour, a bitter aromatic taste, and spec. grav. 1·059. It is formed by the action of aqueous valerianic acid upon glycerine at 527° F.

2. *Butyrines.*—Butyric acid forms three compounds:—

Monobutyrine ($C^{14}H^{14}O^8=C^8H^8O^4+C^6H^8O^6-2HO$) is a neutral, oily, odorous fluid, of a bitter and aromatic taste, and a spec. grav. 1·088; it is formed either at the ordinary temperature, or at 392° F., with an excess of glycerine. When saponified by baryta, it furnishes half its weight of butyric acid.

Dibutyrine ($C^{22}H^{22}O^{12}=2C^8H^8O^4+C^6H^8O^6-2HO$) is a neutral oily fluid, of spec. grav. 1·081; volatile, without sensible decomposition, at 572° F.; soluble in alcohol and æther, and sparingly soluble in water; it is formed either at 527° F., or with aqueous acid at 392° F. When saponified by baryta, it furnishes two-thirds of its weight of butyric acid.

Butyridine ($C^{14}H^{13}O^7=C^8H^8O^4+C^6H^8O^6-3HO$).—This is a neutral, rather thick, oily fluid, of a disagreeable odour, with a spec. grav. of 1·084, and soluble in a solution of carbonate of soda. It is formed by heating to 392° F. a mixture of 1 part of glycerine

and 4 parts of butyric acid. The action of ammonia for five days converts butyridine into butyramide.

3. *Acetines.*—Acetic acid enters into two combinations with glycerine, viz.

Acetine ($C^{10}H^{10}O^8 = C^4H^4O^4 + C^6H^8O^6 - 2HO$) a neutral liquid, with a slightly ætherial odour, and a spec. grav. of 1·20, obtained at 212° F.; and

Acetidine ($C^{10}H^9O^7 = C^4H^4O^4 + C^6H^8O^6 - 3HO$), a neutral odorous fluid, of a sharp taste, which mixes with water, volatilizes at 536° F., and has a spec. grav. of 1·184. It is formed under various circumstances, at 527° or at 392° F., with an excess of either glycerine or acid, aqueous or otherwise. When saponified by baryta, it furnishes glycerine and half its weight of acetic acid.

II. Combinations of Glycerine with various Organic Acids.

1. *Benzoicine* ($C^{20}H^{12}O^8 = C^{14}H^6O^4 + C^6H^8O^6 - 2HO$), a very viscid light-coloured oil, inoxidizable, or nearly so, with a spec. grav. of 1·228, is obtained either at 392° or at 527° F. At 212° F., and even at ordinary temperatures, its formation commences; it is also produced by the action of muriatic acid on a mixture of glycerine and benzoic æther, and even by the direct action of a large quantity of glycerine, at 212° F., upon benzoic æther. Alkalies resolve it into benzoic acid and glycerine; alcohol and muriatic acid, into benzoic æther and glycerine; an effect which is also produced by alcohol alone, either at 212° F., or at the ordinary temperature with the assistance of the air. Ammonia converts it into benzamide.

2. *Sebine* ($C^{32}H^{30}O^{16} = C^{20}H^{18}O^8 + 2C^6H^8O^6 - 4HO$) is formed at 392° F. It is a neutral crystallized substance, and is resolved by oxide of lead into glycerine and sebacic acid.

3. *Camphorine* is neutral, sticky like thick turpentine, and soluble in æther. It is resolved by oxide of lead into acid and glycerine.

III. Combinations of Glycerine with Mineral Acids.

1. *Chlorhydrine* ($C^6H^7ClO^4 = C^6H^8O^6 + HCl - 2HO$).—This substance is obtained by saturating warm glycerine with gaseous muriatic acid, and keeping the solution at 212° F. for thirty-six hours. The solution is then saturated with carbonate of soda, and shaken up with æther, which is afterwards evaporated. The residue is distilled; the chlorhydrine passes over at 440°·6 F. It must be treated with lime and æther. It is a neutral oil, of a pleasant ætherial odour, and a taste at first sweet, and afterwards pungent; its spec. grav. is 1·31; it mixes with water and æther.

It does not immediately precipitate nitrate of silver. It burns with a white flame bordered with green, and muriatic acid is set free. Oxide of lead saponifies it slowly, furnishing quantities of glycerine and muriatic acid, nearly proportionate to the equivalents of these bodies.

All the combinations of glycerine, when prepared by the action of muriatic acid upon the mixture of glycerine and acid, contain chlorhydrine, which cannot be completely separated from them.

Traces of it are also produced by the action of concentrated muriatic acid upon the neutral fatty substances.—*Comptes Rendus*, Sept. 5, 1853, p. 398.

On the Composition of Essential Oil of Thyme.
By M. Lallemand.

The essential oil of thyme, when allowed to stand for some time, deposits a small quantity of stearoptene. This substance forms half the oil; yet its presence in such large quantity has escaped observation.

This *stearoptene*, or *thymole*, is readily obtained crystallized by evaporating its alcoholic solution in the form of rhomboidal transparent tables. It is sometimes deposited in the oil in oblique prisms, with a rhomboidal base, and with supplementary facets on the lateral edges corresponding with the obtuse dihedral angles.

Thymole has a sweet thyme-like odour, and a very sharp peppery taste. It fuses at 129° F., and distils without alteration at 346° F. It may remain fluid for a long time at the temperature of the surrounding atmosphere, but again solidifies on some fragments of the same substance being thrown into it. This phænomenon is one of the causes which has prevented the recognition of the presence of thymole in the products of the distillation of essential oil of thyme. It is very soluble in alcohol and æther, but very sparingly in water, which however does not precipitate it from its alcoholic solution. It possesses no rotatory power, but in the solid state acts upon polarized light in the same manner as doubly refractive media; this is a consequence of its crystalline form. Its formula, derived from five concordant analyses, is $C^{20} H^{14} O^2$. It only differs from the camphor of the *Laurineæ* in containing 2 equivs. less hydrogen.

Thymole is neutral with litmus-paper; it nevertheless combines with caustic potash and soda. At a slightly elevated temperature it dissolves in concentrated sulphuric acid; on cooling, the mixture forms a crystalline mass, which is very soluble in water. This solution, saturated with carbonate of lead or carbonate of baryta, furnishes on evaporation saline crusts, which crystallize in absolute alcohol. From these salts all the other sulphothymates, and sulphothymic acid itself, are obtained. Their formula is $C^{20} (H^{13} S^2 O^5) O^2, RO$; that is to say, sulphothymic acid, like all the analogous vinic acids, is produced by the combination of 1 equiv. of thymole with 2 equivs. of anhydrous sulphuric acid.

Chlorine rapidly attacks thymole in the light. An abundance of muriatic acid is evolved, and a viscous yellowish fluid, of a camphor-like odour, is obtained; this is represented by the formula $C^{20} H^8 Cl^6 O^2$.

Nitric acid also acts very strongly upon thymole, producing resinification. By prolonging the oxidation until the resinous matter has nearly disappeared, an abundant deposit of crystallized oxalic acid is formed.

The property possessed by the stearoptene of combining with cau-

stic potash and soda, is useful in showing its presence in oil of thyme, and in its isolation from the other principles. M. Doveri ascertained that the distillation of this oil furnished two liquids, one of which boils between 347° and 356° F., and the other between 437° and 455° F. The latter consists almost entirely of thymole. It is sufficient, in fact, to throw into this fluid two or three solid fragments of thymole, to cause the whole to form a solid mass in a few days. The portion of oil which distils between 347° and 356° F. still contains more than a third of its weight of thymole. It may be extracted by agitating the product with a concentrated solution of caustic soda, which dissolves the thymole. The oil which floats on the solution is decanted, the compound is diluted with water and saturated with muriatic acid; the fluid thymole soon congeals.

The most volatile portion of the essential oil also contains a considerable proportion of thymole, which may be recovered in the same manner. Its purification however is never complete until it has been distilled several times over caustic potash. In this manner a colourless hydrocarbon is obtained; it has an agreeable odour of thyme, and boils at 329° F.

Thymene is isomeric with essence of turpentine. It has the same density of vapour, and combines with muriatic acid, forming a liquid camphor, identical in composition with the solid hydrochlorate of camphene. Thymene and its compound possess no rotatory power.

It appears therefore that oil of thyme is essentially formed of two principles,—thymene, a hydrocarbon isomeric with turpentine, and thymole, which may be supposed to be derived by substitution from the former. Thus supposing that thymene fixes 4 equivs. of oxygen, whilst 2 equivs. of water are eliminated, we have—

$$C^{20}H^{16}+O^{4}=C^{20}H^{14}O^{2}+2HO.$$

Hence the following bodies would be comprehended in the same molecular type:—

$C^{20}H^{16}$, thymene.
$C^{20}(H^{14}O^{2})$, thymole.
$C^{20}(H^{8}Cl^{6}O^{2})$, chlorated thymole.
$C^{20}[H^{13}(S^{2}O^{5})O^{2}]$, anhydrous sulphothymic acid.

The formula of the liquid oxygenated principle of the essential oil of caraway is identical with that of thymole. The latter will consequently be isomeric with carvacrole. — *Comptes Rendus*, Sept. 26, 1853, p. 498.

On Phosphuret of Titanium. By Mr. Easter.

H. Rose obtained a compound of chloride of titanium with phosphuretted hydrogen. It is a brown amorphous substance, of which Rose states, that when sublimed, it left behind an extremely thin *copper-coloured* coat of metallic titanium. As it has since been shown that the copper-coloured substance obtained in the same manner from the analogous ammoniacal compound is not metallic

titanium, but nitruret of titanium, it appeared probable that the substance obtained by Rose might be phosphuret of titanium.

The author prepared Rose's compound in an apparatus arranged in such a manner, that immediately after its formation it could be driven, in a gaseous form, through a glass tube heated to redness.

In this manner no trace of a copper-coloured substance was obtained, but the glass became coated with a very thin layer of a scarcely soluble gray substance with a semi-metallic lustre; this proved to be phosphuret of titanium. It is characterized by the extraordinarily dazzling lustre with which it burns with fusing nitrate or chlorate of potash. The quantity obtained of it was not sufficient for a quantitative analysis. This substance could not be obtained by heating a mixture of titanic acid, phosphoric acid and carbon, in a charcoal crucible, to a temperature equal to the melting-point of nickel.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 375.

On Propionic Alcohol. By G. Chancel.

M. Gerhardt has long since shown, that the organic substances which he has classed, in consequence of the analogy of their characters and composition, under the name of *homologous bodies*, are produced very often in the same reactions when the conditions under which the latter are accomplished are modified. Thus fatty or albuminous substances, submitted to certain oxidizing influences, give rise to volatile acids (capric, œnanthylic, valerianic, butyric, &c.) homologous with acetic acid, with the aldehydes corresponding to the acids, and to the bibasic acids (suberic, pimelic, succinic, &c.) homologous with oxalic acid, &c. Thus, also, the action of heat upon a multitude of fatty matters furnishes a series of hydrocarbons homologous with olefiant gas.

M. Balard, in his memoir "On the Residues of the Distillation of Grape-marc Alcohol," having shown that these complex products are composed to a great extent of valerianic alcohol, the author was led to think that the other homologous alcohols might also exist in them. By particularly examining the more volatile portions of these residues, the author has extracted from them a new alcohol, *propionic alcohol*, which takes its place between ordinary and butyric alcohol.

Propionic alcohol is obtained by repeatedly rectifying and purifying the first products of the distillation of these residues. After agitating the product with carbonate of potash, in order to dehydrate it as far as possible, it is left standing upon hydrate of potash for twenty-four hours, and then distilled from this substance.

Hydrate of Trityle (the name given by the author to this alcohol) contains—

$$C^5 H^8 O = \left\{ \begin{matrix} C^5 H^7 \\ H \end{matrix} \right\} O.$$

It is a perfectly limpid liquid, lighter than water, and possesses an inebriating fruit-like odour. It is very soluble in water, without however dissolving in it in all proportions. It boils at 205° F. The

density of its vapour is 2·02=2 vols. for the formula above given. It combines readily with sulphuric acid.

Sulphotritylic Acid.—The potash salt of this acid is obtained by saturating the mixture of sulphuric acid and hydrate of trityle diluted with water with carbonate of potash, evaporating to dryness on the water-bath, and treating the residue with boiling absolute alcohol, which dissolves the sulphotritylate of potash. This consists of—

$$C^3 H^7 K SO^4 = \left\{ \begin{matrix} C^3 H^7 \\ K \end{matrix} \right\} O, SO^3.$$

On cooling, the salt is deposited in fine needles, which are anhydrous and exceedingly soluble in water.

Tritylosulphocarbonic Acid is obtained, also in the form of a potash salt, by dissolving caustic potash in hydrate of trityle, and adding sulphuret of carbon to the solution. This salt is deposited in very fine needles.

Hydrate of trityle readily combines with other acids to form compound æthers. The author does not describe these combinations.

In concluding his note, the author calls the attention of chemists to the following equations, accounting for the formation of the various alcohols by the splitting of sugar or glucose under the influence of ferments:—

$$\underbrace{2C^6 H^{12} O^6}_{\text{Glucose.}} = 4CO^2 + 4C^2 H^6 O, \text{ hydrate of æthyle.}$$

$$= 4CO^2 + \left\{ \begin{matrix} C^2 H^6 O, & \text{hydrate of æthyle.} \\ 2C^3 H^8 O, & \text{hydrate of trityle.} \\ H^2 O, & \end{matrix} \right.$$

$$= 4CO^2 + \left\{ \begin{matrix} 2C^4 H^{10} O, & \text{hydrate of tetryle.} \\ 2H^2 O, & \end{matrix} \right.$$

$$= 4CO^2 + \left\{ \begin{matrix} C^3 H^8 O, & \text{hydrate of trityle.} \\ C^5 H^{12} O, & \text{hydrate of amyle.} \\ 2H^2 O. & \end{matrix} \right.$$

He regards the last equation as tending to prove that the formation of hydrate of amyle is necessarily accompanied by the production of the new alcohol.—*Comptes Rendus*, Sept. 5, 1853, p. 410.

On the Preparation of pure Hydrate of Potash. By F. Wöhler.

When nitrate of potash is heated to redness with metallic copper, the nitric acid is completely decomposed, and a mixture of pure potash with oxide of copper is obtained. Pure hydrate of potash for analytical purposes may be very conveniently prepared in this manner, as perfectly pure nitrate of potash is very easily obtained.

One part of powdered nitre takes from 2 to 3 parts of copper. This is employed in the form of ordinary sheet copper, of such a thickness that it may be readily cut into small pieces with scissors. These are put with the salt, in alternate thin layers, into an iron

crucible, which is then covered and exposed for about half an hour to a red heat. On cooling, the mass is treated with water, during which process it becomes very hot; the solution of potash is then poured into a narrow cylinder, where it is left to become perfectly clear, and then drawn off from the deposit of oxide of copper by means of a siphon. It contains no traces of copper. The best method of preserving it free from carbonic acid is that given by Mohr; the flask is closed with a cork, through which is passed a tube, open at both ends, filled with a coarse mixture of sulphate of soda and quicklime.

It is very advisable to employ a copper crucible for this operation, as by the employment of an iron crucible, especially a cast iron one, the potash is rendered a little impure by carbonic and silicic acids. Iron decomposes the nitrate of potash quite as completely as copper; but owing to the presence of carbon, silicium, phosphorus, &c., it cannot be employed in the preparation of perfectly pure potash.

When the copper and nitre are employed in the above proportion, a part only of the former is converted into protoxide. This may be employed a second time in the preparation of potash, by adding to 1 part of nitre 1 part of this oxide and 1 part of metallic copper. It may then be used for the preparation of sulphate of copper.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 373.

On Caprylic Alcohol. By Wladimir Moschnin.

According to a statement of Bouis*, ricinolamide, like ricinolic acid and castor oil, when treated with hydrate of potash, furnishes, with disengagement of hydrogen, sebacic acid ($C^{20}H^{18}O^8$), and a volatile body, which Bouis described as caprylic alcohol, ($C^{16}H^{16}O^2$). In a communication which appeared in the 'Institut,' respecting M. Bouis's investigations, the formula $C^{14}H^{16}O^2$ was attributed to this fluid, which was characterized as œnanthylic alcohol.

If some common castor oil, or ricinolic acid (prepared by the decomposition of castor oil soap by muriatic acid), be mixed with half its weight of hydrate of potash or soda and gently warmed, which is best effected in a copper alembic with a head and a cooling apparatus attached, a strong action soon takes place, which, if the fire be not well regulated, even becomes very violent. The mass in the alembic puffs up without blackening until it becomes four or five times its volume, during which a yellowish oleaginous fluid and water pass over; hydrogen gas is evolved at the same time. The receiver is filled with white fumes of a vapour of difficult condensation, which however is not that of the alcohol, but of another and much more volatile fluid.

The decomposition is generally effected in a quarter of an hour. If the temperature be then raised, products of the decomposition of the soapy contents of the alembic distil over; these apparently con-

* Chem. Gaz., vol. ix. p. 366.

sist of hydrocarbons; they are of a green colour, and smell like petroleum.

If the turbid yellowish distillate contained in the receiver be left standing, it separates into two strata, of which the inferior is watery, the superior oily. The latter is removed with the pipette, and submitted to rectification by itself. It begins to boil at 176° F., when a very inconsiderable quantity of a strong smelling fluid passes over; at 212° F. water goes over; the boiling-point then rises rapidly to 352° F., whilst a limpid oily fluid distils over, which is lighter than water, has a faint aromatic odour, and possesses all the properties ascribed by Bouis to caprylic alcohol. The alembic contains a dark yellow fatty residue, with an acid reaction.

The fluid, obtained pure by repeated rectification, is oleaginous, and not miscible with water; its boiling-point was constantly 352° F. [Bouis gives 356° F. as the boiling-point, with the barometer at 760^{mm}.] On combustion with oxide of copper, and passage of oxygen gas, it gave the following results:—

	I.	II.	III.
Carbon	73·45	73·85	73·61
Hydrogen	13·73	13·76	13·92
Oxygen	12·82	12·39	12·47

Theory requires for—

Œnanthylic alcohol.		Caprylic alcohol.		Average of the analyses.
C^{14} .. 84	72·41	C^{16} .. 96	73·84	73·64
H^{16} .. 16	13·79	H^{18} .. 18	13·84	13·80
O^{2} .. 16	13·80	O^{2} .. 16	12·32	12·55

It therefore corresponds, as may be seen from this comparison, with the numbers found by analysis for caprylic alcohol, and not with those of œnanthylic alcohol. Bouis's first communication to the Academy of Sciences is consequently to be regarded as correct.

The analyses must be performed immediately after the distillation of the alcohol, as the fluid, which is originally limpid and colourless, soon acquires a yellowish colour by standing in vessels containing air; and if then again distilled, leaves in the retort a yellow residue, which is not volatile, and which may easily cause a loss of carbon during the combustion.

In order to settle the equivalent of the alcohol, I have also investigated the baryta salt of the conjugate sulphuric acid observed by Bouis. This acid is best prepared by mixing 2 parts of the alcohol with 1 part of monohydrated sulphuric acid. The Nordhäusen sulphuric acid, the employment of which is recommended by Bouis, furnishes the same product, but in smaller quantity, and with evolution of sulphurous acid. The mixture becomes considerably heated, and acquires a ruby-red colour, probably arising from a compound similar to that observed by Gaulthier de Claubry and Rieckher in the mixture of fusel-oil with sulphuric acid, and characterized by them as oxide of amyle; this is also dissolved in sulphuric acid with a red colour.

The mixture must be gradually effected, with refrigeration, to prevent the evolution of sulphurous acid. The fluid, after mixing, was left standing in a gentle heat; in six or seven days it separated into two strata, of which the lower contained the excess of sulphuric acid, and the upper, which was of a brown colour, the conjugate acid.

Neutralization with carbonates produces from this crude acid the salts of all those bases whose carbonates and sulphates are insoluble, such as lime, baryta and lead. The soluble salts of the conjugate acid may be separated from the insoluble carbonates and sulphates by filtration, and obtained crystallized by careful evaporation.

The fluid filtered from the sulphate of baryta was slowly evaporated on the water-bath. The salt is readily decomposed by boiling; it is remarkably soluble even in cold water, but still more so in hot water. The finest crystals were obtained by cooling the hot concentrated solution during a winter's day to 39°–41° F. Crystals are also obtained by long standing over sulphuric acid, but not *in vacuo*, by which only warty masses are formed.

The crystals are flexible, of a strong bitter taste, and when dried between blotting-paper, have a pearly lustre; in this state they still contain 2 equivs. of water. Dried over sulphuric acid *in vacuo*, they become dazzling white; longer standing decomposes them; they acquire a red colour, and evolve a strong odour, which causes coughing. At 212° F. they are decomposed, becoming black, without fusion. When ignited, they burn with a pale blue flame.

I. 0·7937 grm. of the dry salt, burnt in a platinum crucible with a few drops of sulphuric acid, left a residue of 0·3342 sulphate of baryta.

II. 1·1094 grm., dissolved in water, gave with sulphuric acid a precipitate of 0·4663 sulphate of baryta, or—

	I.	II.
SO^3BaO	42·10 per cent.	42·03 per cent.

Calculation requires for—

Sulphocœnanthylate of baryta.			Sulphocaprylate of baryta.			Average of the analyses.
SO^3BaO	116·5	44·20	SO^3BaO	116·5	41·98	42·06
SO^3	40·0	..	SO^3	40·0		
C^{14}	84·0	..	C^{16}	96·0		
H^{15}	15·0	..	H^{17}	17·0		
O.....	8·0	..	O.....	8·0		

From this the salt analysed is the sulphocaprylate of baryta, the formula of which must however be written with 2 equivs. of water, as this amount was lost *in vacuo*. The formula is consequently $2SO^3\left\{\begin{matrix}BaO\\C^{16}H^{17}O\end{matrix}\right.+2HO$.

Lime and lead salts were also prepared from the crude acid; the former partook of the properties of the baryta salt; it crystallized in white tables, had a bitter taste, and felt soapy.

Oxide of lead forms two compounds with the acid; one, which is

readily crystallizable, is obtained by the saturation of the crude acid with carbonate of lead; it probably contains 1 equiv. of oxide of lead, like the sulphoæthylate and sulphoamylate of lead. The solution of this salt has an acid reaction with litmus-paper. The second compound is obtained by digesting the solution of the former with oxide of lead; a colourless alkaline fluid is produced. By evaporation, a transparent saline mass is obtained, which probably contains 1 equiv. of acid and 2 of oxide of lead. The solution attracts carbonic acid from the air, and becomes covered with a film formed of carbonate of lead, acquires an acid reaction, and passes over by degrees into simple sulphocaprylate of lead.

For the preparation of bromide of capryle, 5 parts of bromine were dissolved in 8 parts of caprylic alcohol, the red solution treated with phosphorus until it was decolorized, and then distilled. The oleaginous distillate, which had an acid reaction, possessed a strong narcotic odour; it was treated with water, in order to separate the bromine compound; the fluid thereby precipitated was washed with a weak solution of carbonate of soda, and then with distilled water, and dried over chloride of calcium. In this state it certainly possessed all the properties of the homologous bromide of amyle; it was heavier than water, did not wet glass, and when heated with potash, furnished bromide of potassium and caprylic alcohol; it could not however be distilled without decomposition, leaving in the retort a black carbonaceous residue; whilst the yellowish distillate, which provoked tears to an extraordinary degree, contained less bromine than is required by the formula of bromide of capryle. When treated with water, it again became colourless, but was of less specific gravity than the original compound before distillation. —*Ann. der Chem. und Pharm.*, lxxxvii. p. 111.

Mode of obtaining Camphor from Oil of Sassafras. *By* M. Faltin.

M. Faltin found that during the action of chlorine gas upon oil of sassafras, the latter becomes converted into a thick tough mass, whilst a large quantity of hydrochloric acid is formed. After neutralization with milk of lime, this mass furnishes on distillation a small quantity of camphor, which is perfectly identical in its properties and composition with common camphor. It could only be obtained from the oil by the action of chlorine. It is probably produced from the unoxygenated oil contained in the oil of sassafras. This observation therefore possesses some interest, as the Sassafras tree belongs to the *Laurineæ*, the same family which includes the Japanese camphor-tree.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 376.

ANALYTICAL CHEMISTRY.

Method of determining the Quantity of Nitrate of Potash contained in Gunpowder. *By* Franz Uchatius.

The author makes use of the following process in his investigations:—

20 grms. of powder are introduced into a flask with about 50 grms. of lead shot; 200 grms. of well-water are then added by means of a graduated pipette; the flask is well closed and shaken for eight minutes, by which the solution of the nitrate of potash in the powder is completely effected.

The solution of nitrate of potash obtained is filtered through gray blotting-paper, and 172 grms. of the filtrate measured off in a second pipette, and placed in a narrow beaker; a thermometer is then placed in it, and the solution brought to the normal temperature (which lies near the ordinary chamber temperature). A glass bubble is now put in; this is so constructed, that when the powder contains 75 per cent.=15 grms. of nitrate of potash, it will rise to the surface, whilst the addition of 3 or 4 drops of water will cause it to sink to the bottom. By means of a graduated pipette, fixed quantities of one of two test solutions are added, so as to cause an increase or diminution in the quantity of nitrate of potash contained in the solution equal to one or more tenths per cent. until the bubble attains the surface of the solution. The per-centage quantity of saltpetre in the gunpowder is now ascertained by adding to or deducting from 75 the amount of diminution or increase in the strength of the solution effected by the addition of the test fluid.

With blast-powders, which contain about 60 per cent. of nitrate of potash, 25 grms. are employed instead of 20; in other respects the process is the same as with other kinds of powder, except that the result obtained, $75 \pm n$, must be reduced by one-fifth.

If the bubble fall rapidly to the bottom, it shows immediately that several parts of nitrate of potash are deficient, so that at least half parts of the stronger test solution may be immediately added; in the same way, if the bubble remain constantly on the surface, the addition of the weaker fluid is indicated.

If too much of one or other of the test fluids be added, so that the normal density of the solution has been overstepped in one direction, this may readily be corrected by an addition in the opposite direction, care being taken that all additions of the stronger fluid are calculated as negative and those of the weaker as positive.

When several determinations are being carried on at once, the operation does not last more than a quarter of an hour, whilst the quantity of nitrate of potash is attained within 0·001.—*Sitzungsber. der Akad. der Wiss. zu Wien, Math. Naturw. Klasse*, x. p. 748.

Test for Aniline. *By* F. Beissenhirtz.

If aniline, or one of its salts, be mixed, even in very small quantity, upon a porcelain plate, with a few drops of concentrated sulphuric acid and a drop of a solution of chromate of potash, the mixture acquires a pure blue colour in a few minutes, very different from that produced by strychnine under similar circumstances. This colour however disappears after a time.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 376.

On the Separation of Nickel from Cobalt. *By* Prof. LIEBIG.

When the mixture of the two oxides is dissolved in hydrocyanic acid and potash, and the solution heated for half an hour in a porcelain dish on the water-bath, or, still better, kept boiling for this time in a flask, the cobalt becomes converted into cobalticyanide of potassium, and the nickel into protocyanide of nickel and potassium. All the cyanogen is extracted from the latter by oxide of mercury, by which the nickel is precipitated in the form of oxide; oxide of mercury produces no change in the cobalt compound. The same end is obtained when, instead of adding oxide of mercury to the cold solution of the mixed cyanides, this is supersaturated with chlorine, and the resulting precipitate of protocyanide of nickel again dissolved by the addition of caustic soda or potash. The chlorine has no action upon the cobalt compound, whilst the nickel compound is decomposed, and all the nickel is at last precipitated as black peroxide.

When an alkali is added to a solution of oxide of cobalt in cyanide of potassium, and the whole is supersaturated with chlorine, it remains clear; the presence of nickel in the smallest quantity causes the production of an ink-black fluid.

This operation must not be performed with heat, as otherwise oxide of cobalt ($Co^2 O^3$) is precipitated with the nickel, and care must be taken that during the introduction of the chlorine the fluid is kept strongly alkaline. The peroxide of nickel thrown down is perfectly free from cobalt.—*Ann. der Chem. und Pharm.*, lxxxvii. p. 128.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Applicability of Molybdic Acid and the Molybdates in Dyeing and Calico Printing. *By* W. H. KURRER.

THE suggestion of Dr. Keller, to substitute for indigo a compound of molybdic acid with protochloride of tin, induced the author to institute some experiments, with the especial view of ascertaining how far there might be any practical advantage in the application of molybdic acid and its compounds in the dyeing of silk, cotton and linen fabrics.

The substance employed in these experiments was obtained from the factory of C. E. Brosche, at Prague, and prepared according to the process recommended by Christl,—melting equal quantities of powdered native molybdate of lead and anhydrous carbonate of soda in an iron crucible, pouring off the molybdate of soda from the fused metal, dissolving in hot water, and boiling with an excess of nitric acid until the molybdic acid separates as a bright yellow powder, amounting, when washed and dried, to a third of the ore.

The molybdic acid thus prepared is not indeed quite pure, but still sufficiently so for any practical application in dyeing.

The double soda salt of phosphoric and molybdic acid is furnished by this factory in the form of a beautifully white crystalline salt, which requires to be preserved in well-closed vessels, on account of its effloresceing in the air.

Dyeing of Silk and Silk Stuffs.—The most intense dark blue colour of the double molybdate of molybdenum and tin is obtained when the silk or silk fabric is impregnated with molybdate of ammonia, then passed in a dry state through an hydrochloric acid bath, and immersed directly, without being washed, in a bath of protochloride of tin, after which it is at once washed and dried.

Lighter blues of all shades, even to the most delicate ash-gray, are obtained when the solution of molybdate of ammonia is proportionately diluted.

Silk and silk fabrics impregnated with a solution of molybdate of soda, dried and then treated in the same way with hydrochloric acid and protochloride of tin, acquire a bright medium blue.

All the shades of colour produced by the compound of a molybdate and protochloride of tin are characterized by extreme durability under the influence of light and air.

The compounds of molybdic acid are not, on the contrary, so well adapted to printing upon silk, as only topical colours can be produced with them.

Dyeing of Cotton Stuffs.—The colours produced upon cotton fabrics by molybdic compounds are inferior and less intense than those communicated to silk. The darkest and purest blue is produced with molybdate of ammonia.

The various tints are all durable, and a white pattern may be printed upon the cotton in the same way as when dyed with indigo by a mordant of chromate of potash and an acid discharge.

Application of Molybdic Dyes to Calico Printing.—Dr. Keller's statements appeared to afford sufficient grounds for anticipating that these compounds would become very valuable materials in printing as well as dyeing. Experience however shows that such is not the case; for when the calico, impregnated with molybdate, is immersed in the hydrochloric acid bath, and even when the acid is concentrated and warm, only a faint yellow tinge is produced, which disappears again completely on washing with water. The washed stuff acquires only a faint blue or gray shade when immersed in a bath of protochloride of tin.

A variety of attempts were made to effect the decomposition of the alkaline molybdates upon cotton and silk fabrics, by means of acetic, tartaric, oxalic and citric acids, &c., and produce a yellow colour upon them; but they were all ineffectual. The stuffs acquired in the protochloride of tin bath only a faint dirty gray, instead of a blue colour.

If therefore the precipitation of the molybdic acid upon the stuffs cannot be adequately effected, and if this acid will not combine with the fibres, so as to resist the solvent action of water, and in both points the author has failed, it is evident that these substances cannot be very extensively employed in printing.

They may be employed for producing a topical colour thus:—A solution of molybdate of soda is mixed with albumen; and after the printing the stuff is dried, and passed first through a bath of warm hydrochloric acid, and then through a bath of protochloride of tin, where the blue colour is developed. Dextrine or tragacanth may be substituted for the albumen.

The topical colour produced by molybdic acid upon cotton stuffs is very durable under the influence of light and air.—Dingler's *Polytech. Journ.*, 1853; and *Pharmaceutical Journal.*

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Hull, September 7th, 1853.

On the Effect of Sulphate of Lime upon Vegetable Substances. By Chevalier Claussen.

About six weeks since I was engaged in making various experiments on the effect of sulphate of lime upon vegetable substances. A portion of the substances then used by me was thrown carelessly aside; and upon returning to my experiments about a fortnight afterwards, I was surprised to find that decomposition had not taken place in those portions of the vegetables which had been subjected to the action of the sulphate, while those which had not been so treated were completely decayed. Among the articles experimented upon were a number of potatoes, each of which was affected by the prevalent disease; some of these remain sound to the present day; the others have some time since completely rotted away. Subsequently I procured some more potatoes, and also some beet-roots, the former being, as far as I could judge, all diseased. I divided the potatoes into three portions. One lot I placed in a vessel with a weak solution of sulphuric acid, and from thence I placed them in a solution of weak lime water. In the second lot the process was reversed, that is to say, the potatoes were first placed in the lime water, and then in the acid. The third lot was left untouched. Ten days afterwards I examined the potatoes, and found, as I expected, that the potatoes which had not been treated with the sulphate were rapidly decaying; those which had been first placed in the solution of lime and then in the acid were more nearly decomposed; while those which had been treated in the mode first described remained as sound as when first taken in hand. Upon being cut open, the diseased part of the potatoes was not found to have spread internally, and the flavour of the root was in no degree affected by the application of the process, nor do I think that its germinating power was injured by the effect of the sulphate. The effect upon the beet-roots was similar to that produced upon the potatoes, and which would seem to be somewhat analogous to that of galvanizing metals, viz. protecting the substances from the effect of atmospheric agencies.

I may add, that muriatic and other acids have been employed by me on other occasions with equal success, the only agents required appearing to be those which will most readily produce a salt in contact with the substances required to be preserved. As at present it does not appear that any means can be successfully adopted to prevent the potato from becoming diseased while in the ground and arriving at maturity, it would certainly be of immense advantage if anything could be discovered by the use of which the roots when taken up could be prevented from that absolute decay and irreparable loss to which potatoes affected by the disease are liable. The results which I have described seem to me to point to the possibility of arresting this loss. How far the plan suggested may be practicable or applicable upon a large scale, my present very pressing and numerous engagements have hitherto prevented me from ascertaining. I do not think that any insuperable difficulty exists with respect to the application of the process. The acid employed by me was very weak, about 1 part to 200 of water; the lime water was about the consistency of milk. The materials are not therefore expensive; and when the value of the crop to be saved is taken into consideration, it would be a matter well-worthy of being tested.—*Athenæum.*

On the Properties and Composition of the Coca Leaf.
By Prof. JOHNSTON.

After describing the remarkable physiological properties of the leaves of this plant, the author explained that they yield to æther a peculiar volatile resinous substance possessed of a powerful odour, in which the peculiar virtues of the leaf are supposed to reside. The plant is as yet to be obtained in too small quantities in this country to admit of a complete chemical examination of the substances which the leaves contain.—*Ibid.*

PATENTS.

Patent granted to T. Greenshields, *for the Manufacture of Alkali.*

IN carrying out his invention, the patentee takes 68 lbs. of sulphate of lime, burned and pulverized, and adds thereto 8 lbs. of fine slack (finely-pulverized coal), mixing them well together. This compound is put into a reverberatory or other suitable furnace, and kept stirred until the whole has become of one uniform dull red heat throughout, care being taken that the temperature be rather lower than a cherry or dull red heat. 60 lbs. of fine-grained salt are now to be added, and the whole well and thoroughly mixed, and the temperature of the furnace is to be raised to a good red, but below a white heat. The mixture will gradually flux and become quite fluid, when it is to be well mixed by raking or stirring, until the mass has become thoroughly heated of one uniform temperature. Pulverized coke is next to be added and well raked in, and in sufficient quantity to separate the fluid mass, and cause it to work freely, without adhering to the rake or instrument used in working.

The temperature is to be maintained until the whole of the chlorine is driven off; and this may be readily ascertained by drawing portions of the charge to the furnace door, as a very small portion of gas escaping may then be seen. When the whole of the chlorine is driven off, the charge is to be drawn from the furnace, and suffered to cool. The sulphate of lime, slack, and coke may be all mixed before putting them into the furnace; but the method before described is preferred.

When the mass has become cold, it is placed in lixiviating vats; the soda salts are dissolved by water, and the solution is allowed to run off through a filter, from the unconsumed carbonaceous and other insoluble matter, into a receiver; it is then to be reduced by evaporation to a salt. The soda salts, so obtained, are to be mixed with fine slack and carbonate of lime, and placed in a reverberatory furnace, known as a black ash furnace, for decomposing the soda salts, and obtaining carbonate of soda, as is well understood.

When the decomposition has been completed in the black ash furnace, the charge is drawn from the furnace, and allowed to cool; it is then placed in lixiviating vats, and the carbonate of soda is dissolved by water. The solution is allowed to run off the unconsumed carbonaceous matter and the insoluble sulphate, and other combinations of sulphur with lime, and the liquid is converted into carbonate of soda, as is well understood. The insoluble residue left in the vats is again used in decomposing salt, as before described.—Sealed Dec. 22, 1852.

Patent granted to P. Warren, *for a Substitute for Papier-maché, &c.*

This invention consists in manufacturing a new material or composition of a character analogous to papier-maché, which is capable of being employed either as a substitute for papier-maché or gutta percha, and its compounds, in forming or manufacturing various articles for which these substances are now used, such as panels and mouldings for railway carriages, trays, picture and other frames, door knobs, buttons, &c., by treating the straw of any fibrous vegetable material in the manner hereinafter described. In order to carry out this invention, straw of any fibrous vegetable substances, such as wheat, barley, oats, rye, and other similar straws, are cut into short lengths by means of any suitable cutting machine. When these straws have any knots, it is necessary to open out and divide the same, which is effected by passing the straw through a pair of millstones, or between crushing rollers; or they may be submitted to the action of any other equivalent apparatus, so that the knots and fibres may be thoroughly and effectually separated and divided. In some cases, either hot or cold water, or other liquid, is applied to the materials under operation, in order to facilitate this process. The cut and divided straw is then boiled in a strong alkaline lye, or solution of caustic alkali, such as soda, potash, &c., until a pulpy mass is produced—which effect will, however, greatly depend on the nature of the straw operated on, and the strength of the alkaline lye or solution which is employed. The mass is then transferred to the machine known in the paper-making trade as the rag-engine,

where it is reduced to pulp in the manner usually practised when operating on rags, &c., in the manufacture of paper. The pulp is then partially dried, in which state it may be pressed or rolled into sheets, or moulded into other forms. These sheets or moulded articles are then dipped into oleaginous or glutinous matter or oil, and are afterwards baked in an oven similar to that employed when manufacturing sheets or moulded articles of papier-maché.—Sealed October 12, 1852.

Patent granted to J. Higgin, *for Improvements in the Manufacture of certain Mordants used in preparing Woven or Textile Fabrics, for printing, staining or dyeing them.*

This improvement consists in the manufacture of a compound mordant, containing oxide or oxides of tin and alumina combined with an alkali, so as to form a solution containing stannite or stannate and aluminate of the alkali employed—soda being the most desirable alkali to use for this purpose. In order to form one of the compound mordants, which the patentee calls "alumino-stannate of soda," perchloride of tin is precipitated by caustic soda, and the oxide is redissolved in more of the alkali, whereby stannate of soda is obtained; and if stannite of soda is required to be obtained also in solution, a little protochloride of tin is mixed with the perchloride before precipitation. To this solution aluminate of soda is now added, which may be made as follows:—Alum is put into a convenient vessel, which may be in such proportion that for every 14 lbs. of metallic tin in the stannate solution there shall be 1 lb. of alumina or oxide of aluminium. To this solution caustic soda is gradually added till all the alumina which was at first precipitated has been redissolved. This is then mixed with the stannate solution, and the mixture is ready for use; or if a dry form be preferred, the solution may be boiled down to a state of dry powder, which will require only to be redissolved in water. In using this mordant, it is diluted to about 12° Twaddell, and the goods are padded in the solution, as is well understood by calico printers. The cloth is then soured with dilute sulphuric acid, as is at present practised with stannate of soda. By this means a compound of alumina and oxide of tin is fixed in the cloth, which, after washing and drying, is ready for printing upon. In some cases it may be convenient to pad the goods in stannate of soda, as at present; and, instead of sulphuric acid, to use dilute solution of an aluminous salt, or to put a portion of an aluminous salt into the sulphuric sours; or the goods may be padded in alum solution first, and afterwards in stannate of soda, souring or not as may be requisite. By any of these means a compound of alumina and oxide of tin will be fixed in the cloth; but it is preferred to use the alumino-stannate of soda, as before described. An acid compound of alumina and oxide of tin is also made, by adding to any of the chlorides of tin, chloride of aluminium, made by precipitating the earth of alum with an alkali, and after washing the precipitate, redissolving it in strong muriatic acid, using about the same proportions between the tin and the alumina as before stated.—Sealed Nov. 24, 1852.

THE CHEMICAL GAZETTE.

No. CCLXVII.—December 1, 1853.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of Butter. *By* Prof. HEINTZ.

SINCE Chevreul's investigation of butter, that substance has been regarded as a mixture of several fats containing glycerine, for when saponified it furnishes various fatty acids, whilst glycerine is separated from all of them. These fatty acids are partly volatile and partly not volatile with watery vapour; partly fluid and partly solid at ordinary temperatures. The former, according to Chevreul, are butyric, caproic and capric acids; the latter, stearic and margaric acids. He considered the fluid acid to be oleic acid.

Lerch has since shown that a fourth acid, caprylic acid, was to be added to the first group; and Bromeis states that the fluid non-volatile acid of butter is a peculiar acid, distinct from oleic acid, and that its solid acid contains no stearic acid, but consists entirely of margaric acid.

As Heintz regards margaric acid as a mixture of stearic and palmitic acids, he was of course led to suppose that stearine and palmitine are contained in butter. This he ascertained with certainty in consequence of Bromeis having sent him a small quantity of the margaric acid prepared by him from butter. He succeeded by partial precipitation with acetate of magnesia in obtaining therefrom pure stearic and margaric acids.

The examination of a considerable quantity of butter has led the author to the following results.

The fluid non-volatile portion of the fatty acids produced by the saponification of butter is not a peculiar acid, butyroleic acid, distinct from oleic acid, as stated by Bromeis, but is completely identical with ordinary oleic acid. It is however very difficult to obtain compounds of this acid in a perfectly pure state directly from the butter. The baryta salt first prepared by the author contained exactly the quantity of baryta attributed by Bromeis to the butyroleate of baryta. By minute separative methods, however, he at length succeeded in obtaining pure oleate of baryta, the composition of which agreed exactly with the formula $C^{36}\,H^{33}\,O^3$, BaO.

From the solid portion of the acids obtained from the butter, the author procured a remarkably large quantity of pure palmitic acid, by the process already described by him for the separation of mixtures of fatty acids. He had however to contend with greater difficulties in preparing the stearic acid, which had been shown by

previous experiments to exist in butter. These difficulties arose, to a considerable extent, from the small quantity of stearic acid existing in butter, but more especially from the circumstance that that substance contains another acid, which is richer in carbon, more difficult of solution in alcohol, and more readily precipitated by acetate of magnesia. This the author was unable to separate in a state of purity, in consequence of the small quantity of it present; he ascertained, however, that it must contain more than 38 atoms of carbon. From his investigations it appears very probable that its composition is to be expressed by the formula $C^{40} H^{40} O^4$. For this new acid the author proposes the name of *butic acid*. The solid portion of butter consequently contains *butine* and stearine in addition to palmitine.

Lastly, the author succeeded in procuring from the fatty acids of butter a small quantity of an acid which fuses between 118° and 172° F., and which, although it was not obtained perfectly pure, agrees so exactly in its properties and composition with myristic acid, that no doubt can be entertained that this acid also is contained in butter. Butter consequently contains myristine.

According to the investigations of Lerch, butter contains compounds of glycerine with—

Butyric acid,	formula	$C^8 H^8 O^4$
Caproic acid,	formula	$C^{12} H^{12} O^4$
Caprylic acid,	formula	$C^{16} H^{16} O^4$
Capric acid,	formula	$C^{20} H^{20} O^4$

The author found in addition compounds of glycerine with—

Myristic acid,	formula	$C^{28} H^{28} O^4$
Palmitic acid,	formula	$C^{32} H^{32} O^4$
Stearic acid,	formula	$C^{36} H^{36} O^4$
Butic acid,	formula	$C^{40} H^{40} O^4$

We thus arrive at the conclusion, that the entire series of fats of the fatty acids, from butyric acid to butic acid, the composition of which may be expressed by the general formula $C^{4n} H^{4n} O^4$, is contained in butter, with the single exception of pichurmeic acid ($C^{24} H^{24} O^4$), and that all those members of the series in which the number of equivalents of carbon are not divisible by 4, but only by 2, do not occur in it; a conclusion already arrived at by Görgey for cocoa-nut oil.

Butter consequently consists of a mixture of oleine with butyrine, caproine, capryline, caprine, myristine, palmitine, stearine and butine.—*Bericht der Akad. der Wiss. zu Berlin*, Aug. 1853, p. 503.

Upon the Crystallizable Matter of the Blood. By C. G. Lehmann.

To his previous communications * upon the nature of the crystals produced from the contents of the coloured corpuscles of the blood, the author adds the following statements, which leave no doubt that these crystals are not forms of a mineral substance, but of an organic body.

* Chem. Gaz., vol. x. p. 273.

First, as regards the conditions necessary for the formation of these crystals, it can only be said at present, that evaporation, which from the manner of their production under a glass plate might be regarded as an essential point in their formation, is without influence upon the separation of the crystals. The dilution of the blood with water, on the contrary, is a not unimportant means of producing the crystallization.

Moreover, if the direct analysis of the crystalline substance had not demonstrated its poverty in mineral matter, even the large quantities of crystalline substance separable from the blood would tell against its being of mineral origin. In the following cases, in which the crystallization was induced under variously modified conditions, the following numbers were obtained for the perfectly dry substance:—

1.	15·25 grms.	Guinea-pig's blood	furnished	0·2428 grm.	or 1·592 p. c.
2.	24·56 ...	...	...	0·9860 ...	4·106 ...
3.	16·54 ...	...	...	0·9105 ...	5·501 ...
4.	16·00 ...	...	...	1·0273 ...	6·421 ...
5.	16·77 ...	...	...	1·1792 ...	7·031 ...
6.	18·38 ...	...	...	1·1937 ...	6·494 ...
7.	21·90 ...	...	...	1·2610 ...	5·758 ...

The differences between these numbers arise entirely from variations in the conditions under which the formation of the crystals was produced in each case. 7 per cent. of crystallizable matter in the blood may however by no means be the highest proportion; nevertheless it follows, even from these determinations, that this substance is one of the principal constituents of the blood, and especially of the blood-corpuscles. Although, however, external conditions exert so distinct an influence upon the quantity of crystals separated, their formation cannot be ascribed to decomposition in the ordinary sense of the word; for in most cases the formation of the crystals was completed within an hour after the death of the animal.

In order first of all to obtain precise data for further investigations, the author limited himself in his quantitative determinations to the blood of the Guinea-pig. The blood was collected from the carotid arteries and jugular veins of animals slightly stupified with æther, and amounted to from 3·7 to 4·3 per cent. of the weight of their bodies.

The crystals usually assume the form of tetrahedra from the blood of the Guinea-pig; sometimes however octahedra, and other forms of the regular system, make their appearance. Their colour is not exactly the same; it is sometimes darker, sometimes paler red; in rare cases, the author has seen them colourless. If the crystals are preserved for a considerable time under water without access of air, they usually acquire a violet colour. In æther and alcohol the crystals lose very little (not quite 2 per cent.). In water they are difficultly soluble; according to the following determinations, 1 part of dry crystalline substance dissolves in about 597 parts of water.

			of solid substance.
1.	42·232 grms. saturated solution cont.	0·0712 grm.	or 0·168 p. c.
2.	52·638	0·0842 ...	0·160 ...
3.	15·672	0·0265 ...	0·169 ...
4.	15·780	0·0245 ...	0·155 ...
5.	13·122	0·0243 ...	0·184 ...

The crystals are rendered insoluble in water by alcohol; they retain their form pretty well, except that their surfaces no longer appear quite plane; they behave nearly in the same manner when gradually heated to 212° F. Reichert found similar coagulated crystals upon the decidua of a pregnant Guinea-pig. For without taking into consideration that the author never observed crystals in the fresh uterus of such pregnant animals, as was the case also with Bischoff (judging from his work upon the ovum of this animal), the properties of the soluble blood-crystals do not agree, as was ascertained by Kunde, with those attributed by Reichert to the crystals found in the uterus. If, however, the crystals which have been treated with alcohol are examined microscopically and microchemically, they will be found to possess all the remarkable qualities described by Reichert. For instance, they swell up in dilute acetic acid to such an extent, that their linear measurement is increased three- or four-fold; on washing out or neutralizing the acid, they return to their former size. They are thus to a certain extent pseudo-crystals, resulting from the coagulation of the original soluble crystallized substance. Reichert may consequently have examined the uterus and ovum of a Guinea-pig which had been lying in spirit for some time. He found the crystals tolerably coloured; and indeed these crystals become considerably darker by coagulation (more by alcohol than by boiling water).

The crystalline substance is very readily decomposed, and indeed equally when completely dissolved, as when kept under water to which the air has access. If the freshly-prepared, bright brick-red, crystalline sediment be allowed to stand from twenty-four to twenty-eight hours in the air at a moderate temperature, it becomes gradually cherry-red, dingy bluish-red, and nearly black, and then begins to deliquesce and to dissolve in the supernatant fluid, to which it gives a dark brown-red colour. When, however, the crystals were no longer mixed with other constituents of the blood, and the supernatant fluid consisted only of the solution of the pure crystals, they frequently remained unchanged under water for eight days, and still longer when the air was excluded. In this way they remain for nine months, as shown by microscopic preparations, which in this period have undergone no change except the acquisition of a violet colour. In the former case, therefore, some more readily decomposable constituent of the blood may act upon them as a ferment, which agrees with the observation formerly made by the author, that fresh blood often evolves sulphuretted hydrogen within six hours after it has been collected, when kept *in vacuo* at a moderate temperature. Moreover, evolution of gas is not to be observed during this transformation of the crystals, either on a large scale or

by microscopic investigation; and absorption of oxygen can only be perceived when several other constituents of the blood are mixed with the crystals.

The morphological changes, which it may be ascertained by means of the microscope the crystals undergo during their chemical metamorphosis, show themselves first in a diminished sharpness of outline; the lively colour generally becomes darker at the same time, and they reflect and refract the light less strongly; their tetrahedric form is still generally to be observed, although individual edges become curved; the whole crystal at length presents the appearance of a hyaline, loose, gelatinous mass, which exhibits considerable tenacity, a property which is entirely absent in the fresh uninjured crystals.

The crystalline substance also undergoes spontaneous decomposition when in complete solution; nevertheless it is also the case here that a pure solution undergoes this process much more slowly than one which still contains other constituents of the blood. The decomposition always commences at the surface of the fluid, which may be readily perceived, because the pure solution of the crystals, which usually has a peach-blossom colour, first becomes dark red and less transparent at the surface, until at last the whole fluid acquires these properties. This not inconsiderable decomposability of the crystalline substance when in solution was moreover the reason why it was necessary to institute many fruitless experiments before the solubility of the crystallizable substance was ascertained in the manner above described; for very frequently a far larger quantity of solid substance was found in the solution than is above stated. In this respect most material differences occurred, which could only be attributed to various degrees of transformation previously induced.

The watery solution of the purest crystals, which moreover exhibits no reaction upon vegetable colours, is coagulable by heat. At 144° F. the fluid begins to become opalescent; at 146° F. the coagulation is completed. Like the coagulated proteine substances, the coagulum is difficult to filter.

The watery solution is not coagulated by æther; when an equal quantity of absolute alcohol is added to it, the fluid only becomes opalescent.

The crystals acquire a dark, almost a black colour, by treatment with concentrated nitric acid; when heated, however, they readily dissolve, first becoming yellow, and forming a yellow fluid. The watery solution of the crystals gives a very considerable, brown, flocculent precipitate with nitric acid.

Muriatic and sulphuric acids, like acetic acid, produce no turbidity in the watery solution, although they change its peach-blossom colour to a pale brownish-yellow. The dry crystals are not dissolved by muriatic or sulphuric acids, but cake into a blackish sticky mass.

The crystallizable substance dissolves very readily in acetic acid with a yellow colour. From this solution it is precipitated in flakes

both by the ferro- and ferridcyanides of potassium. By the neutralization of the acetic acid solution, a dingy pale yellow precipitate is separated.

Caustic potash merely changes the light red colour of the solution to a dingy yellow, without otherwise producing a visible change. The crystals are insoluble in concentrated solution of potash; nevertheless they dissolve very readily in caustic ammonia, forming a solution of a peach-blossom colour; this is consequently the only solvent except water which does not change the colour of the crystals. The substance is precipitated from the ammoniacal solution in a flocculent form by acetic acid, and this even, whilst, the acid being gradually added, the fluid still has an alkaline reaction.

Chlorine gas decolorizes the solution almost instantaneously, producing a white flocculent precipitate. Solution of iodine only changes the colour of the fluid.

Muriate of ammonia, ferro- and ferridcyanides of potassium (without addition of acetic acid), chloride of potassium, chloride of barium, and even neutral acetate of lead, leave the solution completely unchanged. Basic acetate of lead only produces an opalescence, whilst by the addition of caustic ammonia dingy white flakes are precipitated.

Nitrate of silver produces a scarcely perceptible opalescence.

Bichloride of mercury, but only when added in excess, produces a whitish precipitate, which readily dissolves again in a little more of the solution of the crystals; the colour of the fluid remains unchanged in this case, whilst other metallic compounds, such as chloride of iron and bichloride of tin, which moreover produce no precipitates, at least change the colour to yellow. Sulphate of copper produces a pale greenish precipitate, but only after some time.

Nitrate of the protoxide of mercury, as well as bichromate of potash, produce copious white precipitates. Millon's test gave the peculiar reaction of the proteine substances.

Thus whilst the crystalline substance, in its behaviour with some reagents, exhibits the most remarkable analogy with the albuminous substances, it is nevertheless distinguished from every other known proteine compound by its indifference towards other reagents.

Its deportment when heated also distinguishes this substance from most albuminous substances; like these, it begins to be decomposed at 320°–338° F.; it also evolves the so-called horn-like smell, although in a far less degree than these; it also puffs up strongly, but when kindled evolves as much very luminous vapour as though fatty matter were burning.

The investigation of the quantity of water of crystallization contained in this substance did not lead to the result which the author desired. Thus as the crystals are not persistent in the air, it is difficult to determine when they are exactly air-dried, and yet have not lost a portion of their water of crystallization; the microscope is of little use in this case, as on the one hand the material employed for ascertaining the quantity of water is generally very unequally dried, and on the other hand the degree of the efflorescence of the

crystals is difficult to be ascertained under the microscope without the employment of water. The author, indeed, in two exactly coinciding experiments, obtained 19·9 per cent. as the quantity of water contained in the air-dried crystals; yet, in several others, the quantity fluctuated between 15 and 16 per cent. It is moreover worthy of remark, that the substance, dried *in vacuo* over sulphuric acid, lost no more weight at 248° F. in the air-bath. On the other hand, the completely dried crystals, when exposed to moderately damp air at 59° F., attracted on the average of five experiments 11·195 per cent. of water (varying between 11·114 and 11·273 per cent.); consequently the air-dried substance would still contain 10·06 per cent. of hygroscopic water.

Lastly, as regards the quantity of mineral constituents contained in the substance, this is to a certain extent variable, which depends upon the various quantities of iron, or rather of red pigment, contained in the crystals. The results of the quantitative determinations are as follows:—

	grm.		grm.	per cent.	
1.	1·5380	dried substance left	0·0195	or 1·269	of loose, pale yellowish-red ash.
2.	0·5225	... ...	0·0045	or 0·861	of whitish-gray ash.
3.	0·2620	... ...	0·0023	or 0·878	of whitish-gray ash.
4.	0·3379	... ...	0·0041	or 1·213	of yellowish ash.
5.	0·9410	... ...	0·0107	or 1·137	of yellowish ash.
6.	0·7745	... ...	0·0090	or 1·162	of yellowish ash.
7.	0·6588	... ...	0·0049	or 0·744	of gray ash.
8.	0·6851	... ...	0·0055	or 0·803	of gray ash.

These ashes sometimes contained 48 per cent. of oxide of iron with phosphates. The soluble portion has no reaction upon vegetable colours, and contains neither carbonates of the alkalies, chloride of sodium, nor chloride of potassium.—*Berichte der Gesellsch. der Wissensch. zu Leipzig, Math.-Phys. Cl.*, 1852, p. 78.

On the so-called Amorphous Phosphorus. *By* A. Puttfarcken.

The author has examined some amorphous phosphorus obtained from England. He received it in the form of a brownish-red, shining, coherent powder, the peculiar odour of which powerfully affected the eyes.

By long washing with pure water, the phosphorus lost 13 per cent. in weight. The wash-water contained phosphorous and phosphoric acids, and a small quantity of phosphate of lime. The powder, when exhausted by water, was put, when dry and neutral, into well-stopped vessels; it had however again become acid in a very short time.

15 grms. of the so-called amorphous phosphorus were oxidized with nitric acid; this was readily effected without the assistance of heat, merely by the gradual addition of the phosphorus to the nitric acid. 135 grms. of fluid phosphoric acid, of spec. grav. 1·13, were

obtained. Sulphuretted hydrogen, however, threw down so much sulphuret of arsenic from this phosphoric acid, that the quantity of that metal in the phosphorus must have been equal to $\frac{1}{2}$ per cent.

For the sake of comparison, 15 grms. of common phosphorus were converted into phosphoric acid of the same specific gravity. The quantity of acid was 160 grms.

Exposure to a temperature of 392°–437° F. for three days left the amorphous phosphorus unchanged, so that even the microscope could detect no globules of ordinary phosphorus. When heated in a glass tube drawn out to a capillary point, it became black, with evolution of a strong odour of phosphuretted hydrogen, which probably arose from the decomposition of the moist phosphorous acid. It did not fuse during the operation, and on cooling reacquired its original colour. After the tip of the glass tube had been sealed up, the tube was inserted into another a little wider, and then strongly heated for a considerable time with the blowpipe. No sublimate was produced, nor had the substance undergone any change by its exposure to a red heat. Boiled with solution of caustic potash, the substance evolved no phosphuretted hydrogen. Oil of turpentine dissolved much less of it than of ordinary phosphorus.

From this the author concludes that the so-called amorphous phosphorus does not deserve this name. It is rather a low oxide of phosphorus.—*Archiv der Pharm.*, lxxv. p. 136.

On the Chemical Compounds of Copper and Tin, and their Mixtures with one another. By M. Rieffel.

There exist at least seven definite chemical combinations of copper and tin, and the simple law which they follow in their atomic composition leads to the supposition that their number may be still more considerable, as may be judged from the following table:—

		Copper.	Tin.	Colour.
$Cu^1 Sn^\phi$	...	...	...	White more or less approaching that of tin.
	...	...	...	
	$Cu^1 Sn^{48}$	1·11	98·89	
	$Cu^1 Sn^{24}$	2·19	97·81	
	$Cu^1 Sn^1$	34·98	65·02	Iron-gray.
$Sn^1 Cu^\phi$	$Sn^1 Cu^{24}$	92·81	7·19	Golden-yellow.
	$Sn^1 Cu^{48}$	96·27	3·73	Orange-yellow.
	$Sn^1 Cu^{72}$	97·48	2·52	Yellowish-rose.
	$Sn^1 Cu^{96}$	98·10	1·90	Rose.
	...	...	...	...

1. The combination CuSn is remarkable in this respect, that the properties of the two constituent metals are almost completely neutralized in it; so much so, in fact, that it might be said that they had entirely disappeared, were it not for the colour, a sort of grayish-white, which gives it a resemblance to tin, and the property of being denser in a fluid than in a solid state, in which it resembles copper.

It crystallizes in large laminæ, arranged in a very characteristic manner; it is hard, deficient in tenacity, and fuses at 752° F.

2. The group of compounds $Sn^1 Cu^{\phi}$ might be called *cuprides of tin*. In all, the properties of the copper predominate over those of the tin. The compound $Sn\,Cu^{24}$ fuses at an ordinary cherry-red heat, or about 1652°–1832° F. The melting-points of the others gradually approach that of copper. Their crystallization or texture has much resemblance to that of that metal. They are all denser in the fluid state than when solid; all possess great tenacity, greater even than that of copper; they are also harder than copper, and this hardness increases in proportion as the quantity of that metal diminishes; their malleability follows an inverse ratio; that of $Sn\,Cu^{96}$ appears to be greater than that of copper itself.

3. The compounds of the group $Cu^1 Sn^{\phi}$ (*stannides of copper*) have a remarkable resemblance to tin in their general properties. $Cu^1 Sn^{24}$ and $Cu^1 Sn^{48}$ both crystallize in needles radiating in all directions from a great number of different centres; the needles of $Cu^1 Sn^{24}$ are larger than those of $Cu^1 Sn^{48}$.

4. In all the definite combinations of copper and tin, the density is greater than would be deduced by calculation from the densities of the constituent metals, if the volume of the compound be supposed equal to that of the two components; and this result takes place whether the bodies are compared in the solid or liquid state, so that it is independent of the mode of crystallization. From this it may be supposed that the reciprocal action of the copper and tin produces approximation of the molecules.

5. All these definite combinations are difficult to prepare directly in a state of perfect purity, as it is necessary, in order to obtain them in that state, that the degrees of heat at which they are produced should not be sensibly exceeded. The cause of this is that the different compounds require for their formation degrees of heat very nearly approaching one another, so that a certain quantity of some one is always formed as soon as the degree of heat necessary for its production is attained, even when the relative proportions of copper and tin are not such that the whole mass could be converted into that product.

The non-chemical alloys of copper and tin are simple mechanical mixtures of the two chemical compounds between which they stand as to their composition, at least when they have not been overheated (for in this case they also contain a portion of some compound containing more copper). The properties of these alloys or mixtures are always very distinctly deducible from those of their immediate components; this is especially remarkable with regard to the alloys standing between $Sn\,Cu$ and $Sn\,Cu^{24}$, including nearly all those employed in the arts and possessing properties hitherto inexplicable, amongst others—

1. That of being harder and less malleable after annealing than after tempering, which is the reverse of what takes place with steel.

2. That of possessing, in the solid state only, a density superior

to the average of the densities of their immediate constituents ($Sn^1 Cu^1$ and $Sn^1 Cu^{24}$), which is here no longer the effect of an approximation of the molecules caused by a chemical action, but that of mechanical obstacle, which prevents $Sn^1 Cu^1$ from expanding in accordance with its natural impulse, at the moment of its crystallizing in the pores of $Sn^1 Cu^{24}$, which solidifies long before it.

3. That of presenting the maximum of this increase of density in the solid state when it contains about 35–36 per cent. of tin, and the maximum of density itself a little below this composition—a density which surpasses that of copper, and still more that of all the group $Sn^1 Cu^{\phi}$.—*Comptes Rendus*, September 19, 1853, p. 450.

On Lævo-camphoric Acid and Camphor with a Rotatory Power to the Left. By J. CHAUTARD.

The author has obtained from *Matricaria Parthenium* a camphor which deviates the plane of polarization to the left, whilst the camphor of the *Laurineæ* deviates it to the right.

By treating this camphor with nitric acid in the way indicated for the conversion of common camphor into camphoric acid, a new acid was obtained, which deviates the plane of polarization to the left exactly to the same extent that ordinary camphoric acid deviates it to the right, and standing to the latter in exactly the same position as lævo-tartaric acid to dextro-tartaric acid.

These two acids exhibit the most complete identity in their physical properties. If lævo- and dextro-camphoric acids be mixed in equal quantities, they combine immediately, furnishing a new acid completely distinct from its two components, and entirely without action on polarized light. This may consequently be called *racemo-camphoric acid.*

The camphor of the *Matricaria* has the same solubility, the same points of fusion and volatilization, and the same power of rotation as the camphor of the *Laurineæ.*—*Comptes Rendus*, August 1, 1853, p. 166.

ANALYTICAL CHEMISTRY.

On the Volumetrical Determination of Manganese. By G. KRIEGER.

IT is usual in quantitative analyses to separate the constituents of the substances under examination, by taking advantage of their behaviour with various reagents, to convert them, in a certain sequence according to the bodies to be separated, into insoluble compounds, so as to calculate, from the weight of these, the weight of the constituents of the substance.

When, however, the individual constituents of a substance can only be separated from each other imperfectly and with difficulty,

and when it is not desired to obtain an actual separation, but only to determine the relative proportions of the different constituents, another method is employed. A certain quantity of the substance to be examined is weighed, and converted into combinations or products of decomposition of known constitution; from the weight of these and the original weight of the whole, the relative proportions of the constituents themselves are then calculated by the law of chemical equivalents.

Analyses of the latter description are termed *indirect*, in opposition to those of the first, which are *direct*.

On a process of the second description is based the volumetric method, recently put forward by Prof. Bunsen, for the determination of many substances which have hitherto been only separated with difficulty and imperfectly. This method especially furnishes a ready means of distinguishing the higher degrees of oxidation of manganese and similar metals, and ascertaining their quantity. I have, therefore, at the instigation of Prof. Bunsen, endeavoured to ascertain the influence exercised by the various basic oxides at a high temperature upon the protoperoxide of manganese, which is produced by exposure to a red heat in contact with the air, not only to determine the nature of this oxide itself, but especially also to establish the formulæ for the several cases of separation of manganese. As the following investigations would be unintelligible without the knowledge of the above method, I will first describe it shortly.

The principle upon which the whole process is founded is simply this. A quantity of iodine equivalent to the substances to be determined is separated from a solution of iodide of potassium, and this determined by means of sulphurous acid. The separation of the iodine from the solution of iodide of potassium is effected by the addition of muriatic acid to the substance under examination; chlorine is evolved, and passed into the solution of iodide of potassium, by which means every equivalent of chlorine sets free an equivalent of iodine. From this it will be seen that the method can only be employed with a certain class of substances, that is, only with those in which at least one constituent has the property of evolving chlorine when treated with muriatic acid.

For the determination of the separated iodine by means of sulphurous acid, a solution of iodine of known strength in iodide of potassium is necessary; it is to be prepared in the manner described by Prof. Bunsen, and exactly tested as to the quantity of iodine contained in it by bichromate of potash. The sulphurous acid employed should contain at the outside 3 or 4 parts of sulphurous acid to 10,000 parts of water. It is also necessary to have a very dilute solution of starch, which must be perfectly clear, and must have no alcohol added to it. It is best to prepare it fresh every time.

The estimation of the peroxide of manganese is simply effected in the following manner:—A decigramme of the sample is weighed in a small flask, which is then two-thirds filled with pure concentrated muriatic acid; the application of heat causes an evolution of chlorine, which is to be conducted, by means of a tube united to the

employed in an analysis, which gave the following elements of calculation :—

$n=2$, $t'=29{\cdot}2$, $t=49{\cdot}3$, $a=0{\cdot}002685$. $A=0{\cdot}3408$.

When these values are substituted for the letters in the second formula, we obtain—

	Found.	Employed.
$M^3 O^4$	49·92	49·96
$Fe^2 O^3$	50·08	50·04

This experiment therefore shows that the protoperoxide of manganese undergoes no change in its composition by heating to redness with oxide of iron.

II. *Determination of Manganese when in Combination with Alumina.*

The alumina employed in the experiment was prepared in the following manner :—A solution of pure alum, free from iron, was precipitated whilst hot by an excess of carbonate of soda, and digested therewith for some time, in order as far as possible to destroy any basic sulphate of alumina that might be formed. The well-washed precipitate was dissolved in muriatic acid, then precipitated by ammonia, and the precipitate exposed to a strong red heat.

A solution, prepared from 0·5381 grm. of protoperoxide of manganese and 0·4054 grm. of this alumina, was precipitated by carbonate of soda, the precipitate digested for some time with the fluid, then well washed, first by decantation, and afterwards on the filter, dried, and heated to redness. Of this, 0·8358 grm. was made use of in the volumetric analysis; it gave the following elements of calculation :—

$n=5$, $t'=42{\cdot}9$, $t=47{\cdot}5$, $a=0{\cdot}002685$.

If these values be substituted in the second formula, we obtain—

	Found.	Employed.
$Mn^3 O^4$	57·05	57·02
$Al^2 O^3$	42·95	42·98

In this case also the protoperoxide undergoes no change by heating to redness with alumina; and it appears to be a legitimate inference, that those bases which contain 3 atoms of oxygen produce no alteration in the composition of the protoperoxide of manganese when heated to redness with it.

III. *Determination of Manganese in the presence of Glucina.*

0·1500 grm. of pure glucina and 1·2136 of protoperoxide of manganese, when dissolved in muriatic acid and precipitated by carbonate of soda, gave a white precipitate, which when heated to redness acquired the colour of pure protoperoxide of manganese. 0·2502 grm., employed in the volumetrical analysis, furnished the following numerical values :—

$n=2$, $t'=43{\cdot}3$, $t=46{\cdot}4$, $a=0{\cdot}0027272$, $A=0{\cdot}2502$.

would only require to be exposed for a sufficient time to a high temperature with access of air before the volumetric determination. But it appears not impossible that at a high temperature the composition of the protoperoxide of manganese is changed by the action of the stronger bases; the latter displace protoxide of manganese, which is then converted into oxide. In this case the preceding formula must be replaced by the following equation, calculated for oxide of manganese:—

$$x=\frac{a(nt-t')\,.\,Mn^2O^3}{J} \quad \ldots\ldots\ldots\ldots\ldots\ldots (III.)$$

It was consequently necessary to ascertain in what cases the second, and in what the third formula should be employed. For the solution of this question, the following experiments were instituted:—

I. *Determination of Manganese when in Combination with Iron.*

When a solution contains manganese and iron, the quantity of manganese contained in it may be very readily determined in the following manner:—The two metals are precipitated, the iron as oxide, by carbonate of soda, and the precipitate digested for some time on the sand-bath, by which all excess of carbonic acid is expelled and the bases completely thrown down. The precipitate, when well washed, is dried and heated to redness. The quantity of manganese contained in the mixture is now determined by weighing a certain quantity of it, A, putting it into a flask, evolving chlorine by means of muriatic acid, and passing this into the solution of iodide of potassium. The iodine separated is then estimated in the manner already described.

In the first place, a mixture of oxide of iron and carbonate of protoxide of manganese was prepared. The former was obtained in the following manner: clean pianoforte wire was dissolved in nitric acid, the solution freed from the separated carbon and silica, precipitated by ammonia, and the precipitate well washed and heated to redness.

The protoperoxide of manganese employed in this and all the following experiments was prepared from sulphate of protoxide of manganese, which was perfectly free from oxides of copper, iron or cobalt, and had also been purified by repeated crystallizations. The solution of the salt was precipitated by carbonate of soda, the precipitate well washed, dried, and exposed for a considerable time to a red heat with access of air.

A mixture of 0·1898 grm. of this protoperoxide and 0·1901 grm. of oxide of iron was dissolved in muriatic acid, precipitated by carbonate of soda, the precipitate digested for some time with the supernatant fluid, then well washed with boiling water, first by decantation, and afterwards on the filter, dried, and heated to redness in contact with the air for a considerable time. The anhydrous mass obtained was kept in a well-stopped test-tube. Of this mixture, 0·3408 grm. was

employed in an analysis, which gave the following elements of calculation:—

$n=2$, $t'=29{\cdot}2$, $t=49{\cdot}3$, $a=0{\cdot}002685$. $A=0{\cdot}3408$.

When these values are substituted for the letters in the second formula, we obtain—

	Found.	Employed.
$M^3 O^4$	49·92	49·96
$Fe^2 O^3$	50·08	50·04

This experiment therefore shows that the protoperoxide of manganese undergoes no change in its composition by heating to redness with oxide of iron.

II. *Determination of Manganese when in Combination with Alumina.*

The alumina employed in the experiment was prepared in the following manner:—A solution of pure alum, free from iron, was precipitated whilst hot by an excess of carbonate of soda, and digested therewith for some time, in order as far as possible to destroy any basic sulphate of alumina that might be formed. The well-washed precipitate was dissolved in muriatic acid, then precipitated by ammonia, and the precipitate exposed to a strong red heat.

A solution, prepared from 0·5381 grm. of protoperoxide of manganese and 0·4054 grm. of this alumina, was precipitated by carbonate of soda, the precipitate digested for some time with the fluid, then well washed, first by decantation, and afterwards on the filter, dried, and heated to redness. Of this, 0·8358 grm. was made use of in the volumetric analysis; it gave the following elements of calculation:—

$n=5$, $t'=42{\cdot}9$, $t=47{\cdot}5$, $a=0{\cdot}002685$.

If these values be substituted in the second formula, we obtain—

	Found.	Employed.
$Mn^3 O^4$	57·05	57·02
$Al^2 O^3$	42·95	42·98

In this case also the protoperoxide undergoes no change by heating to redness with alumina; and it appears to be a legitimate inference, that those bases which contain 3 atoms of oxygen produce no alteration in the composition of the protoperoxide of manganese when heated to redness with it.

III. *Determination of Manganese in the presence of Glucina.*

0·1500 grm. of pure glucina and 1·2136 of protoperoxide of manganese, when dissolved in muriatic acid and precipitated by carbonate of soda, gave a white precipitate, which when heated to redness acquired the colour of pure protoperoxide of manganese. 0·2502 grm., employed in the volumetrical analysis, furnished the following numerical values:—

$n=2$, $t'=43{\cdot}3$, $t=46{\cdot}4$, $a=0{\cdot}0027272$, $A=0{\cdot}2502$.

would only require to be exposed for a sufficient time to a high temperature with access of air before the volumetric determination. But it appears not impossible that at a high temperature the composition of the protoperoxide of manganese is changed by the action of the stronger bases; the latter displace protoxide of manganese, which is then converted into oxide. In this case the preceding formula must be replaced by the following equation, calculated for oxide of manganese:—

$$x=\frac{a(nt-t')\,.\,Mn^2O^3}{J} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(III.)}$$

It was consequently necessary to ascertain in what cases the second, and in what the third formula should be employed. For the solution of this question, the following experiments were instituted:—

I. *Determination of Manganese when in Combination with Iron.*

When a solution contains manganese and iron, the quantity of manganese contained in it may be very readily determined in the following manner:—The two metals are precipitated, the iron as oxide, by carbonate of soda, and the precipitate digested for some time on the sand-bath, by which all excess of carbonic acid is expelled and the bases completely thrown down. The precipitate, when well washed, is dried and heated to redness. The quantity of manganese contained in the mixture is now determined by weighing a certain quantity of it, A, putting it into a flask, evolving chlorine by means of muriatic acid, and passing this into the solution of iodide of potassium. The iodine separated is then estimated in the manner already described.

In the first place, a mixture of oxide of iron and carbonate of protoxide of manganese was prepared. The former was obtained in the following manner: clean pianoforte wire was dissolved in nitric acid, the solution freed from the separated carbon and silica, precipitated by ammonia, and the precipitate well washed and heated to redness.

The protoperoxide of manganese employed in this and all the following experiments was prepared from sulphate of protoxide of manganese, which was perfectly free from oxides of copper, iron or cobalt, and had also been purified by repeated crystallizations. The solution of the salt was precipitated by carbonate of soda, the precipitate well washed, dried, and exposed for a considerable time to a red heat with access of air.

A mixture of 0·1898 grm. of this protoperoxide and 0·1901 grm. of oxide of iron was dissolved in muriatic acid, precipitated by carbonate of soda, the precipitate digested for some time with the supernatant fluid, then well washed with boiling water, first by decantation, and afterwards on the filter, dried, and heated to redness in contact with the air for a considerable time. The anhydrous mass obtained was kept in a well-stopped test-tube. Of this mixture, 0·3408 grm. was

flask by a piece of vulcanized
of iodide of potassium. One
of chlorine, and this again a
solved in the solution of the i
to it a brown colour.

When the evolution of chlo
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It is now necessary to deter
acid which has been added. T
normal solution of iodine, after
of the solution of starch. If t'
to induce the blue tint, and if
iodine, the quantity of iodine ne
measures of sulphurous acid is x
iodine equivalent to the amount
the quantity of iodine $a \cdot t$, whic
of 1 measure of sulphurous ac
then—

$$x + a \cdot t'$$

and

$$x$$

As 1 equiv. of the iodine set at
of peroxide of manganese, so—

$$MnO^2 : J = x$$

and

$$x = \frac{a(}{}$$

100 parts of the sample conseq

$$\frac{100}{A} \cdot \frac{a(nt-}{}$$

The equation for the estimatic
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manner; it is—

$$x = \frac{a(nt-t}{}$$

If it might be supposed that
manganese from the other oxid
under all circumstances by heati
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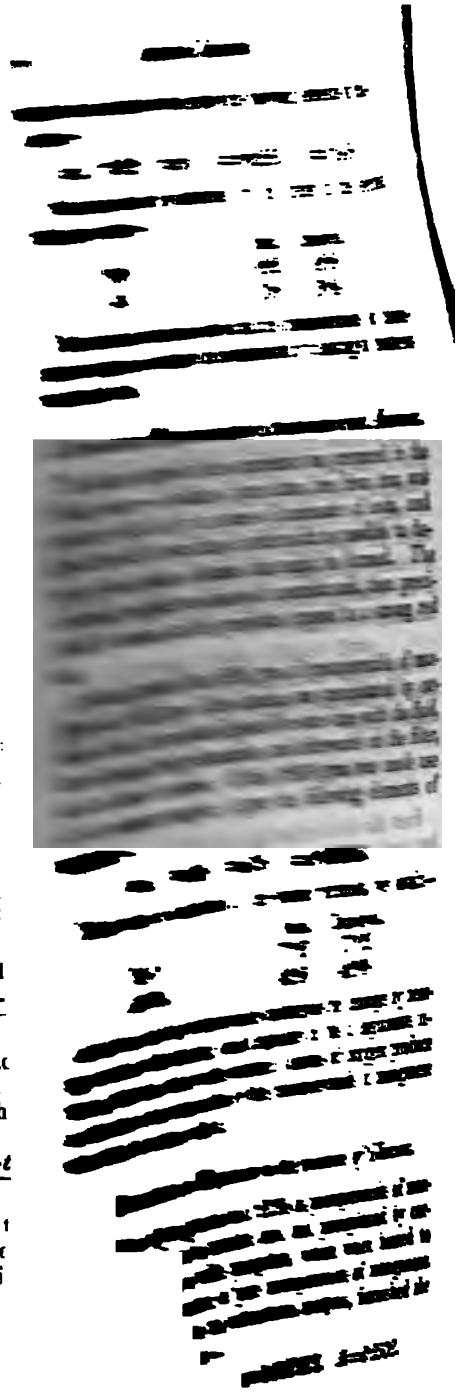
found from the last formula;



When these values are substituted for the letters in the second formula, we arrive at the following proportion:—

	Found.	Employed.
$Mn^3 O^4$	88·99	89·03
BeO	11·01	10·97

As the protoperoxide of manganese, when heated to redness with stronger bases containing 1 atom of oxygen, becomes converted into peroxide, glucina allies itself, in its behaviour towards protoperoxide of manganese, rather with those oxides which contain 2 atoms of metal and 3 of oxygen.

IV. *Determination of Manganese in the presence of Copper.*

To prepare the oxide of copper, pure copper wire was dissolved in nitric acid, the nitrate evaporated to dryness, and the residue heated to redness until the acid was completely destroyed. 0·2232 grm. of this oxide of copper and 0·1267 grm. of protoperoxide of manganese, dissolved in muriatic acid and precipitated by carbonate of soda, gave a precipitate, which was well washed with boiling water, first by decantation, and then on the filter, dried, and heated to redness with access of air. Of this, 0·2824 grm. was employed in the volumetric analysis, from which the following elements of calculation were obtained:—

$$n=2,\quad t'=55{\cdot}5,\quad t=56{\cdot}9,\quad a=0{\cdot}0027272.$$

If these values were made use of in the second formula, x would always be obtained $1\frac{1}{2}$ time too high. The formula III., on the contrary, gave—

	Found.	Employed.
$Mn^2 O^3$	35·23	35·41
CuO	64·77	64·59

From this it is evident that the oxide of copper, as a stronger base, truly replaces the protoxide of manganese, the latter being entirely converted into oxide.

Thus a compound is artificially prepared, analogous to that which occurs naturally in crednerite and black copper.

V. *Determination of Manganese in Combination with Lead.*

The determination is effected in the same manner as in the case of copper. The two oxides are precipitated from their solution by carbonate of soda, the precipitate well washed with boiling water, dried, and then heated to redness in a porcelain crucible. The oxide of lead employed was prepared from pure lead, obtained by heating acetate of lead to redness. The solution of the lead in nitric acid was precipitated by carbonate of soda, the precipitate well washed with boiling water, dried, and heated to redness. A solution of 0·2700 grm. of this oxide of lead and 0·1858 grm. of $Mn^3 O^4$ in muriatic acid, when precipitated by carbonate of soda, furnished a mixture of carbonates of a pale colour, which, when heated to redness in contact with the air for a considerable time, formed a dark yellowish-brown mass. Of this, 0·4619 grm. gave the following numerical values:—

$$n=2,\quad t'=56{\cdot}5,\quad t=84{\cdot}2,\quad a=0{\cdot}0027272.$$

Calculated by formula III., these gave the following result:—

	Found.	Employed.
Mn^2O^3	41·17	41·67
PbO	58·83	58·33

Lead, therefore, as a stronger base, takes the place of the protoxide of manganese, which is converted into oxide.

VI. *Determination of Manganese in Combination with Cadmium.*

Exposure to a red heat with oxide of cadmium also converts all protoperoxide of manganese into oxide, the oxide of cadmium taking the place of the protoxide of manganese. The metals are precipitated from their solution in the same manner as copper and lead. The oxide of cadmium employed was prepared from pure cadmium. 1·4149 grm. of this and 0·2166 grm. of protoperoxide of manganese, dissolved in muriatic acid and precipitated with carbonate of soda, gave a pale precipitate, which, after exposure to a red heat, formed a dark brown-red powder. Of this, 0·9402 grm., employed in the analysis, gave the following elements of calculation:—

$$n=2,\quad t'=21·8,\quad t=48·9,\quad a=0·0027272.$$

These values, inserted in the third formula, give—

	Found.	Employed.
Mn^2O^3	13·87	13·66
CdO	86·13	86·34

VII. *Determination of Manganese in its Combinations with Bismuth.*

The oxide of bismuth employed in the experiments was prepared by heating pure carbonate of bismuth to redness. 0·3624 grm. of this was dissolved in muriatic acid, and mixed with a solution of 0·2477 grm. of protoperoxide of manganese in muriatic acid; both metals were thrown down whilst boiling by carbonate of soda, and the precipitate digested for some time in the supernatant fluid. It was then well washed with boiling water, first by decantation, and then on the filter, dried, and heated to redness in contact with the air; 0·6177 grm. was employed for the volumetric analysis. The following values were obtained:—

$$n=2,\quad t'=52·9,\quad t=100·9,\quad a=0·0027272.$$

Applying these to formula III., we get—

	Found.	Employed.
Mn^2O^3	41·36	41·41
BiO^3	58·64	58·59

Oxide of bismuth, therefore, when heated to redness, exerts the same influence upon protoperoxide of manganese as the oxides of copper, lead and cadmium; in this respect, therefore, it ranges rather with the stronger bases of the constitution RO, than with the feebler compounds R^2O^3.

VIII. *Determination of Manganese in Combination with Zinc.*

The oxide of zinc employed was prepared from pure distilled zinc, in which no other metals were to be detected. The solution of

the metal in nitric acid was precipitated by carbonate of soda, the precipitate well washed with boiling water, dried and heated to redness. 0·3904 grm. of this oxide of zinc and 0·3733 grm. of protoperoxide of manganese were dissolved together in muriatic acid, the solution precipitated whilst boiling by carbonate of soda, and afterwards digested for some time, the precipitate well washed, dried and heated to redness. 0·4754 grm. was employed for the volumetric analysis, and furnished the following elements:—

$$n=2,\quad t'=32·1,\quad t=85·8,\quad a=0·002685.$$

Substituting these values for the symbols in equation III., we obtain—

	Found.	Employed.
Mn^2O^3	49·60	49·72
ZnO	50·40	50·28

In a second experiment, 0·1992 grm. of oxide of zinc and 0·2838 grm. of protoperoxide of manganese were dissolved in muriatic acid, and treated in the manner just described. 0·4278 grm., employed in the analysis, furnished the following results:—

$$n=2,\quad t'=14·9,\quad t=67·3,\quad a=0·002685.$$

Calculated by the formula III.—

	Found.	Employed.
Mn^2O^3	59·53	59·57
ZnO	40·47	40·43

Mn^3O^4, consequently, when heated to redness with oxide of zinc, becomes completely converted into Mn^2O^3.

IX. *Determination of Manganese in the presence of Magnesia.*

The magnesia was prepared from pure sulphate of magnesia, which was quite free from oxide of iron and earths; this was dissolved, precipitated by carbonate of soda, the precipitate well washed with boiling water, dried and brought to a red heat. A mixture of this magnesia with protoperoxide of manganese, dissolved in muriatic acid, and precipitated by carbonate of soda, furnished a white precipitate, which was well washed with boiling water, first by decantation, and then on the filter, dried and heated to redness. 0·2936 grm. of the mixture thus obtained was first employed for the volumetric analysis; and the solution of manganese and magnesia in muriatic acid remaining in the flask was afterwards submitted to analysis. The former process gave—

$$n=2,\quad t'=52·8,\quad t=84·2,\quad a=0·002685.$$

The analysis of the solution furnished 0·1874 of protoperoxide of manganese and 0·2707 of pyrophosphate of magnesia, representing 0·1938 of oxide of manganese and 0·0992 of magnesia. These results give the following numbers:—

	Volumetric analysis.	Ordinary analysis.
Mn^2O^3	66·54	66·01
MgO	33·46	33·78

The oxide of manganese, consequently, in this case also, plays the part of an acid.

X. *Determination of Manganese in the presence of Baryta.*

In order to obtain a perfectly pure baryta salt, chloride of barium was extracted five or six times with alcohol, then dissolved in water, recrystallized twice, and lastly exposed to a slight red heat. A mixture of protoperoxide of manganese and chloride of barium dissolved in muriatic acid gave a white precipitate with carbonate of soda; it acquired a dark brownish-red colour by exposure to a red heat. The volumetric analysis of 0·4597 grm. of this gave—

$$n=2,\quad t'=41\cdot1,\quad t=79\cdot9,\quad a=0\cdot002685.$$

From the muriatic acid solution of manganese and baryta remaining in the flask after the volumetric analysis, 0·1942 grm. of protoperoxide of manganese and 0·3715 grm. of sulphate of baryta were obtained, representing 0·2008 grm. of oxide of manganese and 0·3141 grm. of carbonate of baryta. The analysis of the fluid consequently gives 0·0552 grm. more than the quantity employed. This arises from the carbonate of baryta losing 1 atom of carbonic acid for every equivalent of oxide of manganese present, whilst it was brought into the calculation as an unchanged carbonate. The quantity of oxide of manganese, calculated according to formula III., from the values obtained by the volumetric analysis, amounts to 0·2006 grm. This 0·2006 grm. of oxide of manganese must however expel 0·0551 grm. of carbonic acid, and therefore in fact as much as corresponds exactly with the excess above discovered.

The mass examined contained therefore—

	Volumetric analysis.	Ordinary analysis.
Mn^2O^3	43·63	43·67
BaO	41·72	41·75
$BaO+CO^2$.....	14·65	14·55

XI. *Determination of Manganese in the presence of Strontia.*

To obtain a perfectly pure salt of strontia, chloride of strontium was dissolved in alcohol, by which any chloride of barium would be left behind, the alcoholic solution evaporated to dryness, dissolved in water, and precipitated by carbonate of soda; the precipitate was well washed, again dissolved in nitric acid, the solution evaporated to dryness, and the nitrate thus obtained repeatedly extracted with alcohol to remove the last traces of lime. From the salt thus purified, carbonate of strontia was prepared by precipitation with ammonia. A mixture of this with protoperoxide of manganese, dissolved in muriatic acid, gave a precipitate with carbonate of soda, which was treated as in the preceding experiments. 0·4239 grm. of this precipitate, employed in the volumetric analysis, furnished the following numerical values:—

$$n=1,\quad t'=0\cdot8,\quad t=72\cdot9,\quad a=0\cdot002685.$$

Calculated by formula III., these give 0·1218 grm. of oxide of manganese. The direct analysis of the solution of manganese and strontia remaining in the flask gave 0·1167 grm. of Mn^3O^4 and 0·4163 of sulphate of strontia, corresponding with 0·1207 grm. of oxide of manganese and 0·3346 grm. of carbonate of strontia.

Thus in this case also 0·0314 grm. more than the quantity employed is obtained by the direct analysis; and this arises from the same cause as in the determination of manganese in the presence of carbonate of baryta, that is to say, that every equivalent of oxide of manganese expels an equivalent of carbonic acid. The comparison of the results of the two analyses gives—

	Volumetric analysis.	Direct analysis.
Mn^2O^3	28·60	28·37
SrO.....	18·49	18·42
$SrO+CO^2$	52·91	52·70

XII. *Determination of Manganese in the presence of Lime.*

For the preparation of pure lime, chalk was dissolved in muriatic acid, iron and alumina precipitated from the solution by ammonia, and carbonate of ammonia added to the filtrate. The precipitate obtained was well washed, dried, and heated to redness for a considerable time. A mixture of the lime thus obtained with protoperoxide of manganese was dissolved in muriatic acid, and treated in the usual manner. As, however, carbonate of lime loses a portion of its carbonic acid at a red heat, the precipitate, after calcination, was treated with carbonate of ammonia on the water-bath previous to the volumetric analysis, so as to replace the expelled carbonic acid. Of the mass thus obtained, 0·5723 grm. was employed for analysis, from which the following elements of calculation were obtained:—

$$n=4,\quad t'=41·6,\quad t=51·2,\quad a=0·0027272.$$

Calculated by formula III., these give 0·2801 grm. of oxide of manganese and 0·2922 grm. of lime and carbonate of lime. The direct analysis furnished 0·2721 grm. of protoperoxide of manganese and 0·3694 grm. of carbonate of lime, and therefore in all 0·0785 grm. more than agrees with the supposition that the whole of the lime present in the mixture was in the state of carbonate. If we suppose that the oxide of manganese expels its equivalent of carbonic acid, and combines with the lime thus set free in place of that acid, 0·2721 grm. of protoperoxide of manganese, which by heating with the carbonate of lime becomes converted into 0·2814 grm. of oxide, must expel 0·0774 grm. of carbonic acid, which is almost exactly the quantity supposed to be expelled. The experiments gave the following numbers:—

	Volumetric analysis.	Direct analysis.
M^2O^3	48·94	49·23
CaO	17·13	17·45
$CaO+CO^2$	33·93	33·37

This property of the protoperoxide of manganese, that when heated to redness with stronger bases it becomes converted into oxide, may be very well employed in the preparation of the latter. Thus if the compounds of the oxide of manganese with a base are treated with a weak acid, which will act upon the base without

affecting the oxide of manganese, the latter will be obtained as a residue. The zinc compound is best fitted for this purpose, as the oxide of zinc, even after exposure to a strong red heat, may still be readily extracted by acetic acid. 0·2957 grm. of a product thus obtained, and dried at 302° F., gave the following numerical values:—

$$A=0{\cdot}2957,\quad n=3,\quad t'=46{\cdot}6,\quad t=73{\cdot}5,\quad a=0{\cdot}002685.$$

Calculating from these data according to the formula III., we obtain 0·2938 as the value of x, which differs very little from A.

If we compare the position which has hitherto been assigned to the oxide of manganese in the series of manganic oxides, with its chemical properties as far as they are indicated by the preceding experiments, there can be no doubt that this substance, in opposition to the opinion hitherto entertained, acts rather as an acid than as a base. This oxide, in fact, scarcely occurs as a base in any known salts, except the sulphate and its double salts. All these compounds possess so little stability, that they can only be obtained partially crystallized, and this always with great difficulty; and a mere dilution with water or a slight elevation of temperature is sufficient to destroy the affinity of the acid for the base. On the other hand, the salts just described, in which oxide of manganese makes its appearance as an acid, possess such stability that they completely resist decomposition even when exposed to a strong red heat. Add to this, that, according to the preceding experiments, this oxide can even expel carbonic acid and take its place, and we must arrive at the conclusion that it ought to be called manganous acid rather than oxide of manganese.

By bringing together the results of these experiments, we readily arrive at the method which should be followed in the volumetric determination of the oxides of manganese when mixed with other bodies. If we know only oxide of iron or alumina is present with the compound of manganese, it is sufficient simply to heat the mixture to redness in the air, and to substitute the numbers obtained for the symbols in formula II. But if one of the other oxides above mentioned is present, and the operator is convinced that its quantity is more than sufficient to form a manganous acid salt, the experiment is carried on in the same manner, but with the adoption of formula III.

But if the base present is not in sufficient quantity for the formation of a manganite, or if its quantity be unknown, a certain weight of the substance P is dissolved with half its weight of oxide of zinc, N, precipitated with carbonate of soda, the quantity of the precipitate determined after long exposure to a red heat in contact with the air, and a certain weight p of this made use of for the analysis. If the elements found by this volumetric analysis are designated as above, the per-centage quantity of oxide of manganese in the substance P is obtained from the formula—

$$x=\frac{100\,N}{Pp}\times\frac{a\,(nt-t')\,Mn^2\,O^3}{J}$$

Ann. der Chem. und Pharm., lxxxvii. p. 257.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Products of the Dry Distillation of Organic Bodies. By C. VÖLCKEL.

As a sequel to his previous examination of the products of the decomposition of wood*, and in order to arrive at more exact conclusions on this subject, Völckel has investigated the products of the distillation of sugar. The distillation of the sugar was effected in a copper vessel.

The inflated coal which remained in the vessel, which however is not completely decomposed, amounted to 32–34 per cent., the acid watery distillate to 50–54 per cent. of the weight of sugar, so that about 12–18 per cent. disappears in the form of gas.

The acid fluid (sugar-vinegar) obtained, together with the thick oil which was deposited, was now subjected to distillation. A very volatile yellowish fluid goes over first, consisting of volatile substances which boil below 212° F.; a yellow-coloured oil, which is heavier than water, then follows, with some acid water. During the distillation, the boiling sugar-vinegar acquires more and more colour, and a small quantity of reddish-brown substance is deposited on the sides and bottom of the retort. When a sixth part of the vinegar has distilled over, the separation of the volatile oil ceases, although the acid distillate still smells strongly of it. A thickly-fluid, reddish-brown mass (sugar-tar) remains in the retort.

The Yellowish Fluid which first passes over, when freed from acid by potash and deprived of water by chloride of calcium, begins to distil over at 86° F.; at 122° F. slight boiling commences, but the thermometer rises suddenly to 140° F.; and nearly the whole of the fluid distils over, with a yellowish colour, between 140° and 149° F. The yellowish fluid does not change its colour even by repeated distillation. It possesses a penetrating odour, similar to that of aldehyde. It is readily soluble in water. The watery solution, with addition of ammonia and heat, very readily reduces nitrate of silver. Solution of potash decomposes it, even at ordinary temperatures, into a brown resinous substance, which only dissolves sparingly in free potash. During the distillation of this yellowish fluid with solution of potash, a small quantity of acetone passes over with the water. Only 8 grms. of the yellowish fluid were obtained from 20 lbs. of sugar. The author considers it probable that it consists of acetone and aldehyde.

* Chem. Gaz., vol. x. p. 101.

It is worthy of notice, that amongst the volatile products, neither free wood-spirit, nor pyroligneous æther united with acetic acid, were present.

The Yellow Oil, when purified, rectified and dried over chloride of calcium, distilled over with a yellowish colour at 212° F. At 248° F. slight boiling took place; the thermometer then rose rather suddenly to 320° F. Between 248° and 320° F. about a tenth part of the oil passes over. From 320° the thermometer rose slowly to 323°·6 F., at which it remained a considerable time. At this temperature about half of the oil passes over. The thermometer then rose slowly to 338° F., and lastly to 356° F., at which temperature only a small quantity of strongly-coloured oil remained.

Between 323°·6 and 338° F. somewhat less oil passes over than between 320° and 323°·6 F. The quantity passing over between 338° and 356° F. amounts to about the eighth part of the whole quantity employed for the distillation.

The yellow oil which passes over between 212° and 320° F., of which 20 lbs. of sugar gave 10 grms., was not further investigated by the author by the separation of its component parts. It burnt with a bright reddish flame. It is tolerably soluble in water. It mixes with alcohol and æther in all proportions. Its specific gravity at 59° F. is 1·005. Its watery solution is neutral; mixed with some ammonia, it very readily reduces nitrate of silver with the assistance of heat. If the watery solution be mixed with solution of potash, the fluid, which at first is clear, acquires a yellow colour in a few moments, and immediately afterwards the whole becomes turbid throughout, whilst a yellow substance is deposited, which only dissolves in very small quantity in an excess of solution of potash, but changes under this treatment to a brown colour.

If the oil be brought into contact with a concentrated solution of potash, the action is so violent that the oil begins to boil. If, after the action has ceased, it be distilled with the addition of water, a small quantity of a colourless oil passes over with the water, than which it is lighter, and the whole agrees with the volatile oils of the substance called eupione. The brown substance resulting from the action of potash dissolves in part pretty readily in alcohol, but in part with great difficulty. The portion which is readily soluble in alcohol is completely dissolved by æther with a yellow colour; after the evaporation of the æther, it is obtained as a yellowish-red resinous body, which fuses very readily when heated. The oil is very readily dissolved by concentrated muriatic acid. A decomposition is produced by heat, and the oil becomes changed into a brown substance, which is insoluble in muriatic acid. Concentrated sulphuric acid first of all gives the oil a red colour, and then decomposes it into a black pulverulent substance. The oil is very readily decomposed by concentrated nitric acid. The analysis of this oil (the portion passing over between 284° and 302° F.) gave,—carbon, 63·10; hydrogen, 6·63; oxygen, 30·27.

The oil with a boiling-point of 323°·6 F. is *furfurole*. It has all the properties of this substance, acquires a reddish-brown colour on

being mixed with concentrated muriatic acid, and then deposits a humoid substance of a deep black colour, which consists of 69·81 carbon, 4·02 hydrogen, and 26·17 oxygen. The analysis of furfurole itself gives—

Carbon	62·61	62·62	15 =	1125·00	62·50
Hydrogen	4·46	4·40	6	75·00	4·17
Oxygen.....	32·93	32·88	6	600·00	33·33

The oil which distils over between 323°·6 and 338° F., that especially which passes at 334° F., was also furfurole; it contained a small quantity of oil of bitter almonds. That which went over at 323°·6 F. had a specific gravity of 1·134; that passing at 334° F. was of spec. grav. 1·150 at 59° F. The latter had also a less penetrating odour than the other.

The last portion of the oil which passes over between 338° and 356° F. possesses nearly the same properties as furfurole with a boiling-point of 323°·6 and 334° F. The odour of this oil is however less powerful than that of the two preceding. Its specific gravity is 1·145 at 59° F. Analysis gave 64·08 carbon, 4·72 hydrogen, and 31·20 oxygen. This composition agrees pretty well with the formula of furfurole, $C^{15} H^{6} O^{6}$. From the variation in the boiling-point, it appears that there are several furfuroles possessing the same composition, which only differ from one another by a dissimilar boiling-point. Of these furfuroles, about 200 grms. are obtained by the distillation of 20 lbs. of sugar. The other volatile substances only occur in smaller quantities.

The Sugar-vinegar, from which the volatile oils had been separated by repeated distillation, still had a yellowish colour and a peculiar odour, arising from furfurole, which was still dissolved; this was removed by shaking with æther. This sugar-vinegar contained free acetic acid and a conjugate acetic acid; the latter becomes decomposed at each repetition of the distillation; there remains at last in the retort a small quantity of a dark brown, thickly-fluid substance (sugar-tar), which has at once a bitter and an acid taste, and becomes turbid on the addition of water. The substance thus separated is a bitter fixed body, *assamar*, which is soluble in water, alcohol and æther. The author did not succeed in isolating the conjugate acid or its compounds in a state of purity. The conjugate acetic acid compound is very readily decomposed by strong bases. The separated conjunct, assamar, is changed by the free base into a brown substance, which forms a readily soluble compound with potash, but with lime and oxide of lead one which is difficult of solution. The acid can only remain dissolved by much water, and even then, if long kept, it undergoes partial decomposition even at ordinary temperatures. Its salts cannot be separated from the true acetic acid salts, as like these they are readily soluble in water and alcohol.

Sugar-tar is the name given by the author, as above stated, to the brown and red substances which separate by the distillation of crude sugar-vinegar. They are products of the decomposition partly of the volatile oils and partly of the assamar.

When two-thirds or three-fourths of the crude sugar-vinegar had passed over, the author filtered the dark reddish-brown residue. This was again distilled, the temperature being kept at 248° F. The residue, about 6 per cent. of the crude sugar-vinegar, is a thick fluid, which has an intensely bitter, and at the same time acid taste, the latter arising from the retention of free and conjugate acetic acid by the residue even at 248° F. If this be mixed with a large quantity of water, it becomes turbid, and a reddish-brown substance is separated, which by stirring unites into a soft reddish-brown mass, which collects on the bottom of the vessel. The supernatant watery fluid has a deep reddish-brown colour, with a strong bitter and weak acid taste. If it be evaporated again to a small volume, the addition of water produces a fresh quantity of the reddish-brown substance. This substance is the cause of the colour of the crude sugar-vinegar, and is itself again a product of the decomposition of the assamar.

Assamar, $C^{20} H^{11} O^{11}$, was obtained by the author by neutralization of the fluid with carbonate of soda, evaporating to the consistence of syrup, and extracting the mass with absolute alcohol. From this solution æther still separates a little acetate of soda. The fluid is then evaporated, and the resulting brown syrup dissolved in anhydrous æther. After evaporating the æther, the mass is dissolved in water, filtered, and evaporated under the air-pump. By desiccation under 392° F., the author did not obtain the assamar in the solid form; above that temperature it began to decompose. The watery solution of assamar is neutral; with the addition of ammonia and the assistance of heat, it reduces nitrate of silver. By boiling with bichromate of potash, it acquires a brown colour. Assamar gives no precipitate with acetate of lead; on the addition of ammonia, a yellowish-white precipitate, which is again soluble in a large quantity of water, is produced. When heated, assamar first becomes thinner; it then bubbles up, and when more strongly heated furnishes exactly the same products as sugar with the same phænomena. It is very easily decomposed both by acids and alkalies; it dissolves hydrate of lime; the solution becomes darker in colour when heated, and on evaporation a brownish-yellow substance is separated in combination with lime. The analysis of assamar gave—

	I.	II.	III.	IV.		
Carbon	54·81	54·70	54·65	54·62	20.	54·78
Hydrogen	5·44	5·43	5·38	5·33	11.	5·03
Oxygen	39·75	39·87	39·97	40·05	21.	40·19

Product of Decomposition of Assamar, $C^{20} H^{5} O^{5}$.—The watery solution of assamar, when mixed with potash, immediately acquires a darker colour; when heated to boiling, it becomes deep reddish-brown. Acids separate a brown substance from the cold fluid; this is completely dissolved, with a brownish-yellow colour, in a large quantity of water. It is still more readily soluble in alcohol. If the hot alkaline solution be mixed with an excess of muriatic acid, the substance separated is nearly insoluble in alcohol, and only

dissolves with difficulty in diluted solution of potash. If this brown substance be boiled with diluted muriatic acid, it acquires a dark brown colour, and only a small quantity of it then dissolves in boiling dilute solution of potash. The colour of the substance becomes darker in proportion to the length of the boiling and the strength of the muriatic acid. The brown substance, which is obtained by boiling for two hours and a half, by which some formic acid is formed, swells up when dilute solution of potash is poured over it. The fluid filtered from it was deep brown. The residue on the filter, when washed, proved to be a difficultly-soluble potash compound. The potash was removed by treatment with dilute muriatic acid; this also attaches itself obstinately to the substance. The substance, when completely washed and dried, possesses a fine brown colour. It is insoluble in water or alcohol. When moist, it reddens litmus-paper. When potash or ammonia is poured over it, it takes up these bases, and then dissolves in small quantity in water. Judging from all its properties, the brown substance is an acid insoluble in water, the salts of which, even with an alkali as base, are but sparingly soluble in water. Analysis:—

Carbon.....	61·36	12 =	900·00	61·53
Hydrogen	4·60	5	62·50	4·27
Oxygen	34·04	5	500·00	34·20

If a solution of assamar be boiled with dilute muriatic acid, a small quantity of formic acid and a brown substance are produced; the latter, when washed with water and treated with a dilute boiling solution of potash, behaves like the preceding body. Its composition is as follows:—Carbon, 64·63; hydrogen, 4·58; oxygen, 30·79.

If stronger muriatic acid be employed, the brown substance is obtained darker in colour and of the composition of the ulmine of sugar. The author found the numbers given in the first column:—

		Mulder.		
	I.			
Carbon	65·72	65·27	65·64	65·44
Hydrogen....	4·52	4·52	4·50	4·38
Oxygen.....	29·76	30·21	29·86	30·18

Assamar, therefore, when boiled with dilute acids, furnishes similar products to sugar. For comparison, the author boiled sugar with dilute muriatic and sulphuric acids. The fluid distilled off contained also some formic acid. The brown humus-like substance produced in this manner, Mulder's ulmic acid, the author explains to be a mixture of various brown substances, of which that which is soluble in alcohol appears to be identical with that precipitated by water from sugar-tar. Another has the composition $C^5 H^2 O^2$; a third, nearly that given by Mulder for humine. The decomposition which the sugar undergoes during boiling with acids is nevertheless different from that of assamar. The principal decomposition depends upon the expulsion of oxygen and hydrogen in the form of water from the sugar. Glucic acid, $C^8 H^5 O^5$, is first of all formed from the sugar, and from this apoglucic acid, $C^{18} H^{10} O^{10}$. By con-

tinued boiling, two brown substances of different tint are last of all produced; these are both acids. The first, which only occurs in small quantity, forms with potash a compound which is readily soluble in water; the other, with the same base, one which is nearly insoluble in that fluid. A second subordinate decomposition then takes place, in which formic acid and a reddish-brown substance, which is soluble in alcohol, are formed. The latter contains more hydrogen than is necessary to form water with its oxygen; this, however, by continued boiling, is again changed by the acid into a substance which is insoluble in alcohol and potash. It can then no longer be separated from the brown substance belonging to the first decomposition of the sugar. The boiling of sugar or assamar with acids consequently almost always produces mixed brown substances, of a somewhat different colour in every experiment; in these oxygen and hydrogen no longer exist in equivalent proportions.

The reddish-brown substances of the Sugar-tar.—These are deposited during the distillation of the crude sugar-tar on the sides and bottom of the vessel; they are products of the decomposition of the volatile oils, furfurole, &c., and of assamar. Another portion of the reddish-brown substances is separated by water from the sugar-tar; this has a soft consistence, in consequence of an intermixture of assamar. The assamar is extracted by boiling water, and there remains a solid, brittle resin. This substance consists of a reddish-brown resin, which is soluble in æther, and a reddish-brown substance, insoluble in æther, but pretty soluble in alcohol.

The latter does not soften in boiling water, but dissolves therein in small quantity. Its alcoholic solution has a fine reddish-brown colour, reddens litmus-paper, and furnishes a yellowish-brown precipitate with an alcoholic solution of acetate of lead. For analysis, the reddish-brown substance was dissolved in alcohol, the solution evaporated at the temperature of the atmosphere, and the residue dried at 212° F. The analyses gave—

Carbon	61·03	61·63	60·01	60·51	62·04	62·62	63·40
Hydrogen ..	5·44	5·33	5·05	5·03	5·05	4·96	5·13
Oxygen	33·53	33·04	34·94	34·46	32·91	32·42	31·47

From this the author concludes that this substance has been produced from the assamar by separation of water and formic acid. The same substance is also obtained in small quantity by boiling sugar or assamar with dilute muriatic acid. It is the substance which is called acid pyroresin in wood-tar; and it is to this substance principally that wood-vinegar, as well as sugar-vinegar, owes its peculiar colour.

The decomposition of sugar by dry distillation is explained by the author in the following manner:—The sugar first, when heated above its point of fusion, or to a temperature of 410° or 438° F., passes into caramel, $C^{12} H^9 O^9$, with loss of 2 equivs. of water.

If the temperature be raised to 482° F., a slightly acid water with a little furfurole distils over from the caramel. No permanent gases however are evolved at this temperature. The residue of the sugar,

which has been exposed to a temperature of 482° F., is still for the most part soluble in water with a dark colour (caramel). The portion which is insoluble in water is black, inflated, insoluble in alcohol, and only soluble in very small quantity in solution of potash.

The author calls this substance *caramelan*, to distinguish it from other similar substances. Its analysis gave—

Carbon	55·09	24 =	1800·00	55·17
Hydrogen	5·14	13	162·50	4·98
Oxygen	39·77	13	1300·00	39·85

During the formation of caramelan from caramel, 5 equivs. of water are expelled from 2 equivs. of caramel, $C^{24}H^{18}O^{18}=C^{24}H^{13}O^{13}+5HO$. From 482°–572° F. the conversion of the caramel into caramelan becomes still more complete; but at the same time the decomposition of the caramelan commences with formation of furfurole, acetic acid, the conjugate acetic acid and water. The formation of these substances increases by further increase of heat, by which the caramelan becomes converted into substances always growing richer in carbon, until at last at a red heat gaseous compounds of carbon are produced.

The solid and fluid fixed bodies, which are formed in sugar-vinegar, wood-vinegar and wood-tar, are not, in the author's opinion, distilled over, but carried up mechanically by the watery vapour and gases.—*Ann. der Chem. und Pharm.*, lxxxv. p. 59.

Examination of Bassorah Galls. By Dr. L. F. Bley.

The author has examined the so-called Bassorah galls. They were treated consecutively with alcoholic æther, cold water and hot water.

The galls lost 12 per cent. of water in drying. The alcoholic ætherial extract left a residue equal to 17 per cent. on the weight of the galls, of which water dissolved 14 per cent. The portion which was not soluble in water was shaken with æther, which took up 3 parts of a yellowish fatty oil of a mild taste. The portion insoluble in æther was a brown solid resin; it had a shining appearance, was hard and brittle, burnt when heated over flame, fused, and left a small residue of earthy ashes. The alcoholic solution gave a grayish-white flocculent precipitate with water; it dissolved in caustic alkalies with a fine red colour, and in fatty ætherial oils. Concentrated sulphuric acid dissolved the resin, forming a reddish-brown fluid. Nitric acid gave a yellowish solution. The portion of the galls not taken up by æther was exhausted with alcohol, the alcohol distilled off, and the residue treated with water, by which 5 parts of the resin above mentioned were separated. The tannic acid was precipitated by solution of gelatine; in this manner 60 parts of tannic acid and 8 parts of gallic acid were obtained; these were determined by their behaviour with salts of oxide of iron.

Adding the constituents contained in the watery extracts, the Bassorah galls consist of—

Tannic acid	130	parts
Gallic acid	8	...
Fatty oil	3	...
Resin	17	...
Extractive with salts	10	...
Lichen-starch with small portions of common starch and albumen	42	...
Fibrine	230	...
Water	60	...
	500	parts.

Archiv der Pharm., lxxv. p. 138.

On a Modification of Hydrogen. By G. Osann.

Osann has observed, that when moistened blue or red litmus-paper is laid upon thin plates of common or amalgamated zinc, it exhibits after some time acid as well as alkaline reactions. He ascribes this phænomenon to the circumstance that the salts contained in the litmus are decomposed by the poles of the resulting secondary circuit. In order to test this reaction further, he now laid the same test-papers, moistened, upon six metallic plates, namely, zinc, iron, lead, copper, tin and silver, taking care to keep them wet. The results were,—with zinc, as before; with iron, alkaline reaction, brown spots of oxide of iron were alone to be perceived on the blue test-paper; with lead, strong alkaline reaction; with copper, alkaline reaction; with tin, slight alkaline reaction; with silver, no reaction. That alkaline reactions alone were observed upon the four metals arises not from the base alone acting, but from the blue papers being less sensitive to acid than the red ones to alkaline reactions.

The author then tried whether water is decomposed by such circuits. With this view, the following two experiments were instituted. A small rod of amalgamated zinc was introduced into a glass tube closed at one end by fusion. A solution of neutral sulphate of zinc was next poured into the tube, which was then placed with its open end downwards in the same fluid. The same process was adopted with a small piece of iron and a solution of protosulphate of iron.

A day after the commencement of the experiment small gas bubbles were to be seen upon the surface of either piece of metal. This formation of gas bubbles was repeated every day. In the course of three weeks a sufficient quantity of gas for examination had collected in the upper part of the tube. On examination, it appeared to be hydrogen gas. At the same time, small black spots of oxides might be observed both on the zinc and iron. The black spots on the iron were more striking than on the zinc; the evolution of gas was also stronger with the iron. The iron, when examined by the lens, appeared as though it were marbled, that is to say, black and pale spots were uniformly distributed over its whole surface. After these experiments, it cannot be a matter of doubt that the water is decomposed, and that in consequence of this decomposition the metals

had become oxidized, and a separation of hydrogen gas had taken place.

From this experiment Osann concludes that the secondary circuits produced must also have an influence during the solution of metals in acids, and thinks he can better explain the decomposition of water then produced as taking place by such influence, than by the supposed predisposing affinity. At the same time he takes into consideration the catalytic action. The above-described decomposition of water appears under the external form of catalytic action, and may evidently be referred to the secondary currents.

Lastly, with regard to the theory of the hydro-electric circuit, it appears from the above experiments that it is unnecessary, in a chemical point of view, to suppose a particular arrangement of the atoms of the fluid before the completion of the circuit, and then shifting according to the right and left side of the circuit after its closure. By the action of the secondary current of the readily oxidizable metal, the electrolyte which is in contact with it is decomposed, and the positive constituent, which *in* the above cases is the hydrogen, is eliminated at its surface.

With regard to the hydrogen which is generated by decomposition at the poles of the battery, the author says that it must be a modification different from those known.

Thus when dilute sulphuric acid is decomposed by the electric current, employing platinum for the positive pole and carbon for the negative, if the current be not too powerful, the evolution of hydrogen at the carbon commences later than the evolution of oxygen at the platinum. The carbon consequently takes up a certain quantity of hydrogen in its pores, so that the gas is only evolved on the surface after the pores are filled with it. If the carbon, after hydrogen gas has been evolved from it for some time, be introduced into a solution of nitrate of silver, metallic silver is immediately precipitated upon its surface. Now as hydrogen in its gaseous state does not possess this property, and as carbon also does not produce any decomposition of this salt, there is nothing left but to suppose that the hydrogen in this case is in some peculiar state, by virtue of which it is enabled to effect the decomposition of oxide of silver. This state evidently corresponds with that in which oxygen becomes ozone; the author consequently proposes to characterize these two modifications by naming the form produced by electricity the *electrical*, and the other the *thermal* modification. Against this view the objection may be raised that the reduction of the silver may be effected by the carbon, which might have obtained a reducing power by serving some time as a negative electrode. That this however is incorrect appears from the following experiment:—Spongy platinum also has the property of retaining hydrogen during the decomposition of water by the electric current, so that gas is only evolved upon its surface after some time. For the success of this experiment, however, it is necessary that the current be not too strong. If now the spongy platinum, which has been some time employed in dilute sulphuric acid as a negative electrode, be intro-

duced into a solution of nitrate of silver, silver will also be separated. The separated silver may be detected with the lens. In order that there might be no mistake, however, the platinum foil, to which the spongy platinum was attached by means of platinum wire, was washed with water after it had been in the solution of nitrate of silver, until the last washing-water, when tested with muriatic acid, gave no silver reaction; it was then put into nitric acid, and, after being kept there some time, assisting the action of the acid by heat, it was taken out, and muriatic acid added to the fluid. The silver reaction immediately appeared. There can be no doubt consequently that hydrogen, in the state in which it exists in the pores of the carbon and platinum, is a peculiar modification, in which it is capable of producing an immediate deoxidizing action.

Admitting this supposition of the author, we have now three allotropic conditions of hydrogen as well as of carbon, namely, 1st, common hydrogen, which may be united with oxygen by platinum; 2ndly, that prepared in the dry way, which, according to Faraday, does not combine with oxygen; 3rdly, the modification just described by Osann.—*Journ. für Prakt. Chem.*, lviii. p. 385.

On the Action of Carbonic Acid upon Quinine and Cinchonine, and on the Formation of Crystallized Carbonate of Quinine. By M. Langlois.

A stream of carbonic acid gas was passed through newly precipitated quinine and cinchonine suspended in water. The prolonged action of the gas causes the quinine and cinchonine to dissolve; the former dissolves more readily than the latter. Both solutions, when exposed to the air, lose a portion of their carbonic acid, the one furnishing crystals of carbonate of quinine, the other merely cinchonine. Crystallized carbonate of quinine is very readily obtained in this manner by the following process:—

10 grms. of sulphate of quinine are dissolved in distilled water, to which a few drops of sulphuric acid have been added. The addition of ammonia to the solution precipitates the quinine, which is collected on a filter and washed, and then diffused, whilst still moist, through a litre of water. The milky fluid is put into a glass vessel, into which well-washed carbonic acid gas, produced by the action of muriatic acid upon marble, is passed. The quinine is entirely dissolved in less than an hour. The solution, although supersaturated with acid, retains an alkaline reaction.

Quinine combines directly with carbonic acid without dissolving, when it is not suspended in a sufficient quantity of water. By the process just described, a perfectly limpid solution is obtained, from which, after a short exposure to the air, crystals of carbonate of quinine are deposited; these continue increasing in size for twenty or twenty-four hours. After this time no more is deposited, although the liquid still contains the salt. Spontaneous evaporation only furnishes quinine, which is also instantly precipitated by ammonia, potash and soda. Lime-water produces the same effect, with formation of a deposit of carbonate of lime.

The solution of carbonate of quinine consequently furnishes at first crystals of the saline compound, whilst afterwards this compound is destroyed, giving rise to carbonic acid and quinine. There is a complete analogy between these phænomena and those presented by a solution of carbonate of cinchonine. The latter never furnishes crystals, because the salt is present in very small quantity; this no doubt depends on the solubility of cinchonine in water being very little increased by the intervention of carbonic acid.

Carbonate of quinine forms transparent acicular crystals, which soon effloresce when exposed to the air; they are soluble in alcohol, but insoluble in æther; they render reddened litmus-paper blue. With acids they produce a brisk effervescence.

At a temperature of 230° F. they are decomposed; carbonic acid is evolved, and the quinine remains without alteration. It only fuses at 338° F. The decomposition of carbonate of quinine at so low a temperature furnishes a ready means for its analysis in the following manner:—A glass tube, 12 or 15 centims. in length, and closed at one end, was weighed, and 0·399 grm. of carbonate of quinine introduced into it. It was then connected, by means of a cork covered with india-rubber, with a bent tube, which passed under a graduated bell-glass placed over some mercury in a test-glass. The extremity of the tube passed the surface of the metal, so as to reach into the empty part of the bell-glass intended for the reception of the carbonic acid gas. The closed tube containing the salt was then heated in the oil-bath to about 230° F. Just before this temperature is reached, the carbonate of quinine is decomposed, the carbonic acid being driven off without any sensible change being produced in the physical characters of the salt.

The 399 milligrms. of the salt employed in this experiment furnished 21·36 cub. centims. of carbonic acid gas at 32° F., and a pressure of 76 centims. This volume of gas weighs 0·0422 grm. The evolution of gas ceases long before the oil-bath reaches the temperature of 338° F., at which the quinine fuses and entirely loses its water. The moisture which adheres to the sides of the tube is readily removed by means of a few pieces of blotting-paper. The weight of the quinine, obtained by weighing the tube after the experiment and deducting the weight of the empty tube, was 321 milligrms. 0·399 grm. of carbonate of quinine consequently furnished—

	Grm.	Per cent. Found.	Per cent. Calculated.
Quinine	0·3210	80·45	80·21
Carbonic acid	0·0422	10·58	10·88
Water	0·0358	8·97	8·91

These numbers lead to the formula $(C^{20} H^{12} NO^2, HO) CO^2 HO$ for this salt. Six successive experiments on different quantities of the salt all led to the same results. As it must be regarded as neutral, we thus, in ascertaining its composition, fix the equivalent of quinine, which in this case agrees with that admitted by Liebig.

This decomposition of carbonate of quinine at a low temperature has also shown that this salt is not formed by double decomposition when a saline solution of quinine is treated with a solution of carbonate of potash or soda. The precipitate formed consists only of quinine, which always retains a larger or smaller quantity of the carbonate employed, in spite of repeated washing. It is to the presence of this that the precipitate owes its property of effervescing with acids; but when fused in a glass tube, it does not furnish the least trace of carbonic acid. The same applies also to cinchonine, and perhaps even to all vegetable bases.—*Comptes Rendus*, Nov. 7, 1853, p. 727.

Note on Caproic Alcohol. By M. V. F. Faget.

Caproic alcohol is a limpid, aromatic, very refractive liquid, insoluble in water. Its specific gravity, when fluid, is 0·833 and 0·754 at 32° and 212° F.; the density of its vapour is 3·53. Its composition agrees with the formula $C^6 H^{14} O$.

At an elevated temperature, potash converts it into caproic acid, with evolution of hydrogen; the analysis of the silver salt led to the formula $C^6 H^{11} AgO^2$.

3 or 4 grms. of a specimen, mixed with amylole, treated again with sulphuric acid, gave a sulpho-salt, which crystallized in scales. This salt, which was in too small a quantity to be completely purified, furnished 40·4 per cent. of sulphate of potash.

A similar quantity of a sample collected between 309° and 331° F., treated with bichromate of potash and sulphuric acid, furnished caproic acid and an oil boiling about 320° F., the density of the vapour of which is 7·34, whilst its composition agrees with the formula $C^{13} H^{26} O^2$. This would be that of caproic æther, of œnanthylic alcohol, or of the œnanthylic æther of caproic alcohol.

Other portions, collected between 331° and 383° F., possessed a density of vapour and furnished analytical results indicating mixtures of œnanthylic alcohol, $C^7 H^{16} O$, with the caprylic alcohol of Bouis, $C^8 H^{18} O$.

The purest portion of this alcohol was collected between 298° and 309° F. Deficiency of material prevented the preparation of its æther.—*Comptes Rendus*, Nov. 7, 1853, p. 730.

ANALYTICAL CHEMISTRY.

On the Volumetrical Determination of Copper and Oxalic Acid. By Francis Leeshing, Esq.*

The methods for the determination of copper hitherto proposed are more or less tedious and complicated, with the exception of two, which recommend themselves by more expedience. The one, which consists in estimating the copper in its ammoniacal solution by

* Communicated by the Author.

means of the colorimeter, is however only of value when the materials to be tested do not vary to a great extent in their respective amount of copper. The other, a volumetrical method, based on the reaction which takes place between suboxide of copper, bichloride of iron and hydrochloric acid, and assisted by the application of permanganate of potash, for determining the quantity of protoxide of iron formed, has been proposed quite recently by Dr. H. Schwartz (Chemical Gazette, May 2, 1853), and is certainly very valuable, especially when other metals are present along with the copper, although it is somewhat complicated.

The following very simple mode of valuation will be of service when the copper salt or its solution is free from other metallic or earthy admixtures. It is based upon the property which copper solutions possess, when rendered slightly acid by pure nitric or sulphuric acid, of imparting by their oxidizing action a purple or blackish tint to a strip of white paper saturated with a solution of hydriodate of potash and boiled starch, which reaction ceases the moment the copper has been completely precipitated. The latter object is best effected by oxalic acid, neutralized with potash or by neutral oxalate of potash, as the light blue shade of the oxalate of copper thus obtained does not interfere with observing the point, when the iodine paper ceases to be coloured.

79·35 grs. of crystallized oxalic acid ($C^2O^3, HO + 2Aq$) correspond to 50 grs. of pure oxide of copper, or 99·4 grs. of oxalic acid to 50 grs. of metallic copper.

In an experiment, where 100 grs. of pure oxide of copper had been dissolved in nitric acid (free from nitrous acid), and precipitated with pure oxalic acid, which had been previously neutralized with potash, 158·5 grs. of oxalic acid were required; the calculated number is 158·7.

In applying the common Centigrade alkalimeter, we dissolve, according as we intend to obtain the per-centage of oxide of copper or of metallic copper, either 79·35 grs. or 99·4 grs. of pure crystallized oxalic acid in distilled water, neutralize it with potash, and fill the alkalimeter by addition of water to the top line of the graduations. Of the salt to be tested, on the other hand, 50 grs. are dissolved in 1 or 2 oz. of water; and to this the solution contained in the alkalimeter is cautiously added, until the iodine paper dipped into the mixture ceases to be coloured; each measure consumed will thus correspond either to $\frac{1}{2}$ a grain of oxide of copper or $\frac{1}{2}$ a grain of metallic copper, according as the alkalimeter has been made up with 79·35 or with 99·4 grs. of oxalic acid.

It is obvious that a copper salt will serve, *vice versâ*, for the determination of oxalic acid in its combinations with alkalies; and for this purpose the sulphate of copper is the most suitable, 100 grs. of which represent 50·5 grs. of crystallized oxalic acid.

The above method will allow a valuation of copper sufficiently accurate for most purposes, if care is taken that the solutions are not too acid nor too diluted. But besides it must be observed, that the paper saturated with a mixture of hydriodate of potash and

boiled starch yields the purple reaction, not only with copper salts, but likewise with hypochloric and nitrous acids (though not with nitric or sulphuric acids, except when these are employed in a concentrated state). The salts of the peroxide of iron exercise a similar effect, whilst deoxidizing agencies, such as sulphurous acid, are apt to interfere with the reaction.

The hypochlorites, in contradistinction from the nitrites, produce the purple reaction on the above paper whether the liquid is alkaline or acid, whilst the nitrites react only when the acid is set free. To ascertain the presence of hypochlorites and of nitrites, we proceed accordingly in the following manner:—A small portion of the copper solution to be examined is precipitated by caustic potash, adding so much of the latter that the liquid acquires an alkaline reaction when the copper is separated by filtration, and the filtered liquid examined with the iodine paper for chlorine; when no indication of the latter is shown, pure sulphuric acid is added in excess, and the liquid tried again for nitrous acid.

The chlorine or hypochlorous acid can be removed most effectually by adding a few drops of the tincture of galls or of catechu, by which large quantities of chlorine are instantly converted into hydrochloric acid, whilst the reaction of the copper is not interfered with so long as the liquid is not heated. The nitrous acid may be destroyed by addition of urea or nitrate of urea, when the two mutually decompose themselves into nitrogen and carbonic acid*. Sulphurous acid, when present, may be oxidized by treatment with nitric acid.

Small admixtures of lime (for instance, 1 part of lime to 24 parts of oxide of copper), magnesia, and even of zinc and nickel, have scarcely any influence upon the result, as the two first remain in solution so long as the liquid is acid, whilst zinc, and still more nickel, are only precipitated after some time.

It was likewise found that gum, sugar, dextrine, alcohol, when present, do not alter the result.

Busby, near Glasgow,
December 5, 1853.

Note on an Apparatus for the Determination of Carbonic Acid. *By* M. S. DE LUCA.

The apparatus consists of,—1st, a tube, in which the decomposition of the carbonate is effected; 2nd, a tube, in which the air is deprived of its humidity and carbonic acid; and 3rd, two other pieces of apparatus, the object of which is the retention of all the carbonic acid arising from the decomposition of the substance under analysis. These four pieces of apparatus may be indicated by the letters A, B, C and D.

* Nitrate of urea is easily prepared by evaporating a quantity of urine, and adding subsequently a large proportion of nitric acid. When allowed to stand for about twelve hours, a crop of large crystals of nitrate of urea is obtained, which are to be purified by recrystallization.

The apparatus A consists of a tube closed at one end, and contains a smaller tube, also closed at one end, into which the carbonate, having been previously weighed, is put. This little tube communicates on the one hand with the U-shaped washing apparatus B, the office of which is to furnish a current of dry air free from carbonic acid; and on the other, with some concentrated sulphuric acid, placed in the bottom of the large tube A. The communication between the two pieces of apparatus A and B may be intercepted by means of a peculiar stopper, formed of a very small tube closed at one end, and into which a small india-rubber tube is inserted. On the other hand, the apparatus A communicates with an apparatus C with five bulbs, of which the lower one, which is elongated at the two extremities, has a capacity of 5 cub. centims.; the two middle ones each contain 10 cub. centims., and the two upper have double the capacity of the middle ones. Into this apparatus 15 cub. centims. of a concentrated solution of potash are introduced.

The few traces of carbonic acid which might escape the action of the solution of potash are finally condensed in the tube D, which is filled with small pieces of potash, and communicates with C.

The apparatus B is composed of a U-shaped tube, containing in one of its branches a potash tube, and in the other some pumice-stone and sulphuric acid. The corks of the U-shaped tube are closed with sealing-wax, as is also that of the apparatus D. The cork of the apparatus A is partially covered with sealing-wax.

These four pieces of apparatus are put together in a very simple manner; the author employs for this purpose small glass tubes, open at both ends, containing india-rubber tubes. This mode of closing tubes, or establishing a communication between several pieces of apparatus by means of glass tubes containing tubes of vulcanized india-rubber, is more convenient than the employment of free india-rubber tubes, and fixing them to the glass tubes by means of silk threads, as is done in organic analyses.

A platinum wire is attached to each apparatus, with the double purpose of facilitating the manipulation during weighing, and of fixing it upon a wooden support.

The following is the mode of operation:—After weighing the three pieces of apparatus, A, C and D, the communication between A and B is intercepted in the manner above described; the three pieces of apparatus are united, and a portion of the air contained in the whole apparatus is then sucked out through the tube D. In this manner the sulphuric acid comes in contact with the carbonate, and decomposes it; the carbonic acid during its evolution bubbles at first through the sulphuric acid, and leaves its humidity there, and then passes into the portions C and D, where it is condensed. When the reaction is completed, the communication between A and B is opened, and air is again drawn through the apparatus; in this manner a current of dry air is produced, which carries with it all the carbonic acid from the apparatus A to be deposited in C and D.

On weighing the apparatus now, the loss of weight in the apparatus A shows the quantity of carbonic acid contained in the sub-

stance analysed; and this loss ought to correspond with the increase in the weight of the pieces C and D.

With the same apparatus A, with some modifications, the quantity of carbonic acid in a bicarbonate may be determined, as well as the water which this bicarbonate may lose under the influence of heat.—*Comptes Rendus*, Nov. 7, 1853, p. 730.

PATENTS.

Patent granted to W. Brown, *for an improved method of treating Coal and Bituminous Substances, and for Improvements in the Treatment of their Volatile Products.*

The first operation consists in distilling the coal, or other bituminous matter, in conjunction with steam, at a dull red heat; and, for this purpose, the coal or other bituminous matter is introduced into a retort fitted with a steam-pipe, so situated as to become red-hot by passing through the furnace. This steam-pipe terminates in the closed end of the retort; so that when the retort is charged with coal or other bituminous matter, and the furnace is in action, the steam-pipe becomes red-hot,—and steam being then passed along it, this also becomes red-hot, and in this state enters the end of the retort, and rapidly unites with and expels the volatile matters arising from the coal or other bituminous matter; by which means their decomposition into gas is wholly or in great measure prevented, and the amount of oily or condensable product greatly increased.

The steam-pipe may, if preferred, be passed through a furnace, distinct and separate from that which heats the retort; which arrangement admits of the withdrawal of the fire from the retort, or the diminishing of its intensity at pleasure, without altering the temperature of the steam-pipe. By this means the distillation of the coal or bituminous matter can either be continued altogether or in part, with the retort at a temperature below that of a dull red heat. The steam-pipe may be of cast iron, or of cast or wrought iron, glazed or enamelled, as it is termed, or it may be of clay or earthenware. In distilling, a condenser is employed as usual, the temperature of which should not be lower than 50° F.

A quantity of volatile products having been thus obtained from coal or other bituminous matter, these are again subjected to distillation, in a still or other convenient vessel, with or without the employment of a steam-pipe, though the use of steam is preferred when a large amount of paraffine is required; but where the production of oil is the chief object, steam may be dispensed with. When steam is used, it is to be brought into the still, in a superheated state, by passing it through a red-hot steam pipe, disposed in the furnace or flue of the furnace which heats the still. The steam enters through the upper part of the side of the still, and promotes, as before, the distillation of the volatile matters, whilst it retards their destruction

or conversion into gaseous or other worthless compounds. By this means the paraffine and heavy hydrocarbonaceous oils are preserved.

During the progress of the second distillation, it will be observed that the products vary at the different periods of the distillation; and these are therefore to be kept separate, or received in different vessels. At first a thin oil or impure eupione oil comes over to the extent of about one-eighth of the total fluid employed; after this a thicker and heavier oil, containing paraffine, makes its appearance, to the extent of from 40 to 50 per cent. of the fluid employed; and lastly, a thick butyraceous matter is evolved, consisting chiefly of paraffine, but mixed with heavy oil; and this continues to the end of the operation, and constitutes about one-fourth of the bulk of the fluid originally used.

These three products are treated as follows:—The impure eupione oil is mixed with from 5 to 10 per cent. of its weight of oil of vitriol or sulphuric acid, to which an equal bulk of water is added; bichromate of potash is next thrown in, equal in weight to one-half of the sulphuric acid employed; the whole is then heated in any convenient vessel of wood, lead or earthenware, and during the heating the materials are diligently stirred together. As soon as the temperature has reached 212° F., the heating means may be withdrawn, and the whole permitted to cool and settle.

The eupione oil is next to be decanted from the acid fluid, and treated with a warm solution of caustic soda; the whole being well mixed, and afterwards left at rest for some time to settle. Lastly, the eupione oil is decanted from the alkaline fluid, and distilled, either alone, or with water, or steam, as is practised with respect to volatile oils generally. The heavy oil, containing paraffine, is next treated either with strong sulphuric acid and peroxide of manganese, in the proportion of 10 per cent. of acid and 5 per cent. of peroxide of manganese, or it is subjected, like the eupione oil, to the action of the sulphuric acid and bichromate of potash, in the same manner and proportion as indicated for the eupione oil; after which it is treated with soda ley, and allowed to settle. The heavy oil is then decanted and distilled in the usual way; the first portions being added to the eupione oil, as consisting chiefly of that substance; the second, and by far the larger portion of the whole, is received apart under the name "lubricating oil;" whilst the last portions, being thick and of the consistence of butter, are mixed with the impure paraffine, which results from the third stage of the second distillation of the crude products, and which are next treated as follows:—Having allowed the impure paraffine to remain for twenty-four hours, or longer, in a cool place, to crystallize, the oily mixture is placed in a bag or filter, similar to those in use for the separation of spermaceti from sperm oil. When the oily fluid has drained away, the paraffine is removed to a press and subjected to severe pressure, as is practised with respect to stearic acid by the makers of that substance. It must then be melted, and when cold again pressed, the oil being in both cases added to the drainings, which are to be treated as explained under the head "heavy or lubricating

oil." The paraffine must now be melted, and the heat raised to about 400° F., when strong sulphuric acid is to be carefully stirred into it in the proportion of from one-twentieth to one-tenth of the weight of paraffine operated upon. After boiling for a few minutes, the fire must be withdrawn, and the charred oil of the paraffine allowed to settle in the form of a black powder from the melted paraffine. This being separated, the paraffine must be boiled in water or in a weak solution of soda; after which it may be cooled, and is fit for the market.—Sealed Jan. 13, 1853.

Patent granted to J. Booth, *for an Invention for manufacturing Chromate and Bichromate of Potash from Chromic Iron or Chrome Ore.*

This invention consists in reducing the oxide of iron in chrome ore, either wholly or in part, by means of carbon in any of its several forms, or by means of any of its compounds, which are or may be employed as fuel, such as carbonic oxide or carburetted hydrogen. This operation forms the first stage of the manufacture. The second operation consists in removing, by means of sulphuric acid, the iron that has been reduced by the first part of the process. The remainder of the process of manufacture is similar to that which is now in use, namely, to heat the residue obtained by this improved process, in contact with carbonate of potash, and either with or without saltpetre.

In carrying out his invention, the patentee takes the ore known as chromic iron or chrome ore, and grinds it to a powder by the usual mechanical means. This powdered ore he mixes with about one-fifth of its weight of powdered charcoal, and places it upon the hearth of a reverberatory furnace, constructed as the reverberatory furnaces for reheating or puddling iron are ordinarily constructed, that is to say, in such a manner that the heat or flame may be as free as practicable from uncombined oxygen or atmospheric air. By this operation, the greater part, or all of the oxide of iron in the chrome ore will be decomposed, and the iron reduced to the metallic state. When one charge of the mixture has been reduced, as above described, it is to be raked out, and a second charge of the mixture must be introduced into the heated furnace, reduced in its turn and replaced by a third charge, and so on. Each charge, when raked out of the furnace, is to be thrown into vats containing dilute sulphuric acid, whereby the iron is dissolved, and a solution of protosulphate of iron or copperas is thereby formed. This solution (still containing free acid) is to be drawn off and run upon a fresh charge of reduced ore, in order more fully to saturate the free acid, after which it is again to be drawn off, and evaporated to crystallization, so as to produce copperas in a state adapted for commerce. The residue in the vats is then to be well washed with water and dried, and afterwards mixed with carbonate of potash and saltpetre, and heated in the same manner that the chrome ore itself is heated in the process usually employed.—Sealed Nov. 9, 1852.

INDEX TO VOL. XI.

ACETIC acid, new methods for manufacturing pure, 96.
Acetines, 122, 425.
Acetone, chemical examination of, 341.
Acetonic acid, 345.
Acetstannæthyle and compounds, 149.
Acids, anhydrous organic, 136, 211; on some organic, 231; contained in fungi, 291.
——, fatty, on the use of, as a source of light, 175.
Acrylic acid, 232.
Æsculine, preparation and properties of, 301.
Æthers, on the combinations of the æthylic and methylic with certain metallic chlorides, 361.
Æthylamine, action of, on oil of mustard, 71; new double salt of, 94.
Æthyle, on the preparation of crude pelargonate of oxide of, 144.
Æthylurethane, 408.
Æthylstannæthyle, 111; compounds of, 153.
Aldehyde, on the constitution of, 46.
Alkali, improvements in the manufacture of, 438.
Alkalies, on the quantitative determination of the, in the siliceous minerals not soluble in acids, 252, 333.
Alkaloids of the cinchonas, on the, 321.
Alum, on the employment of the ashes of boghead coal in the manufacture of, 169.
Ammonia, action of, on certain metallic arsenites, 229; the action of, on the sulphoamylate of lime, 326; determination of the, contained in waters, 317.
Amyllammine, 326.
Angelic acid, anhydrous, 211.
Aniline, test for, 434.
Anthropic acid, 41.
Antimony, fluorine salts of, 1; action of, upon certain classes of salts, 329; reduction of, by means of cyanide of potassium, 399.
Antimony and sulphur, on the isomeric combinations of, 290.
Arbutine, preparation and constitution of, 61.
Arctostaphylos Uva-Ursi, examination of the leaves of, 61.
Arctuvine, preparation and properties of, 63; arctuveine, 64.
Arsenic, action of, upon certain classes of salts, 329; reduction of, by means of cyanide of potassium, 399.
Arsenious acid, researches on, 364.
Arsenites, action of ammonia upon some, 230.
Assamar, 464; products of decomposition of, 465.
Azobenzide, observations on, 32.
Babo, L. von, on sinapine, 81.
Barreswil, M., on photography upon stone, 275.
Barruel, G., on a new alloy of silver, 15.
Baryta, manufacture of caustic, 387.
Becquerel, A., on the composition of milk, 164.
Bee, examination of the food of the queen, 91.
Bees, remedy for the stings of, 36.
Beet-root, composition of, 154.
Beissenhirtz, F., on a test for aniline, 434.
Bennett, E. T., on the determination of phosphoric acid, 17.
Benzoicine, 122, 425.
Berberine, new salts of, 70.
Bertagnini, C., on the compounds formed by some essential oils with the alkaline bisulphites, 46.
Berthelot, M., on the combinations of glycerine with acids, 121, 421; on the action of ammonia on the sulphoamylate of lime, 326.
Bischoff, Prof., on the production of urea, 287.
Bleaching liquors, mode of testing the strength of, 139, 419.
Bley, Dr. L. F., examination of Bassorah galls, 467.
Blood, on the crystallizable matter of the, 442.
Blood-corpuscles, constituents of the, 348.
Bog iron ore, analysis of, 276.

Boletic acid, 291.
Bolley, Dr., on a process for determining the value of soap, 55; on the determination of water in commercial iodine, 118; on the acids contained in fungi, 291; on the recovery of gold and silver from the fluids employed for electro-plating and gilding, 354.
Bone, improvements in the production of ornamental surfaces on, 59.
Booth, J., on the manufacture of chromate and bichromate of potash from chrome ore, 478.
Booth, Prof. J. C., on the analysis of cast iron, 368, 388, 411.
Boracic acid, influence of water upon, in borates, 65; existence of, in various natural substances, 113; combinations of, with oxide of silver, 232; with baryta, strontia and magnesia, 194; with metallic oxides, 214; with the oxides of lead and copper, 270; with oxide of iron, 404.
Boussingault, M., on the conditions under which fresh bread becomes transformed into stale, 47; on the determination of the ammonia contained in waters, 317.
Brass, fire-proof bronze colour for, 119.
Brazil, J., on improvements in the preparation of dye-woods, 19.
Bread, on the conditions under which fresh becomes transformed into stale, 47.
British Association, proceedings of the, 414, 437.
Brodie, B. C., on the formation of hydrogen and its homologues, 297.
Bromine, separation of iodine from, 75.
Bronze, fire-proof, for copper and brass, 119.
Brown, W., on the volatile products from coal and bituminous substances, 476.
Brunnquell, R., on the preparation of crayons for writing on glass, 193.
Buff, H. L., on nitruret of iron, 229; analysis of pig iron and bog iron ore, 276.
Bunsen, R., on the preparation and properties of magnesium, 114.
Butic acid, preparation and composition of, 442.
Butter, on the composition of, 441.
Butyric acid, 147.
Butyrines, on the, 424.
Caffeine, new salts of, 70.
Cahours, A., on stanmethyle, 292.
Calico-printing, applicability of molybdic acid and the molybdates in, 435.
Calvert, Prof. F. C., on soaps, and their employment in manufactures, 115.
Cambacérès, J., on the use of fatty acids as a source of light, 175.
Campbell, D., on the presence of formic acid in the human secretions, 310.
Camphor, from oil of sassafras, 433.
Camphorine, 425.
Caproic acid, anhydrous, 211.
Caproic alcohol, 472.
Caprylic acid, anhydrous, 88.
Caprylic alcohol, 430.
Caramelan, properties and composition of, 467.
Carbonic acid, apparatus for the determination of, 37, 474.
Carbothiacetonine. 344.
Carlet, H., on sebacic acid, 324.
Carvacrole, 227.
Carvene, 226; carvole, 227.
Casaseca, M., on hydrated chloride of magnesium, fused and in powder, 384.
Cast iron, on the increased strength of, produced by the use of improved coke, 158.
Chancel, G., on propionic alcohol, 428.
Chautard, J., on physaline, 15; on lævo-camphoric acid and camphor with a rotatory power to the left, 450.
Chemical Society of London, proceedings of the, 139.
Chiozza, L., on anhydrous valerianic acid, 52; on anhydrous caprylic and pelargonic acid, 88; on a combination of pelargonic acid with deutoxide of nitrogen, 123; on the anhydrous acids, 211; on some organic acids, 231.
Chlorhydrine, preparation and properties of, 425.
Chlorine, separation of, from iodine, 75; new method for determining the amount of available, contained in hypochlorites of lime, soda or potash, 419.
Christl, M., on the manufacture of pure acetic acid, 96.
Chrome ore, on the manufacture of chromate and bichromate of potash from, 478.
Cinchonicine, properties and constitution of, 321.
Cinchonidine, action of heat upon, 323.
Cinchonine, action of carbonic acid on, 470.
Citrate of iron and quinine, adulteration of, 269.
Citric acid, products from the fermentation of, 147.
Claussen, Chevalier, on the effect of sulphate of lime upon vegetable substances, 437; on improvements in the manufacture of some saline and metallic compounds, 20.

Cnicine, 15.
Coal, on the volatile products from, 476.
Cobalt, on the allotropic modification of oxide of, 91; researches on, 201; separation of, from nickel and zinc, 380, 435.
Coca leaf, properties of, 438.
Copper, fire-proof bronze colour for, 119; new processes for determining, 176, 276, 472; combinations of, with cyanogen, 326; separation of, from zinc and nickel, 379; from mercury, 380.
—— and tin, on the chemical compounds of, 448.
—— and zinc alloys, on the analysis of, 259.
Coriander oil, constitution of, 16.
Cotton, detection of, in unbleached linen, 99.
Coumaric acid, 232.
Crayons for writing on glass, 193.
Crystals from the sea-coast of Africa, description of, 418.
Cyanic æthers, products of decomposition of the, 407.
Cyanogen, estimation of, by volume analysis, 296.
Cynuric acid, researches on, 315.
Debus, H., on oxylizaric acid, 316.
Dessaignes, V., on physaline, 15.
Diæthylurea, 407.
Dienst, M., on a fire-proof bronze colour for copper and brass, 119.
Dubrunfaut, M., on the manufacture of beet-root sugar, 385; on the manufacture of caustic baryta, 387.
Dufau, A., on some combinations of copper with cyanogen, 326.
Dyeing, on the applicability of molybdic acid and the molybdates in, 435.
Dyes, means of detecting the, which have been used in the dyeing of stuffs, 218.
Dye-stuff, new, from China, 221.
Dye-woods, preparation of, 19.
Easter, Mr., on phosphuret of titanium, 427.
Elaylstannæthyle, 109; compounds of, 131.
Elbers, C., on the preparation of molybdic acid from the native molybdate of lead, 181.
Ericineæ, chemistry of the plants of the family, 187.
Ericinole, preparation and properties of, 65.
Ericoline, preparation and constitution of, 14.
Eupione, on the manufacture of, 476.
Faget, V. F., on caproic alcohol, 472.
Fairbairn, W., on the increased strength of cast iron produced by the use of improved coke, 158.
Faltin, M., on camphor from oil of sassafras, 433.
Fat, analyses of the constituents of, 383; on the synthesis of the proximate principles of the animal, 421.
Filhol, E., on the existence of boracic acid in various natural substances, 113.
Flajolot, M., on the separation of some metallic oxides, 379.
Flandin, C., on a new method of analysis for the organic poisons, 215.
Flax, gases evolved in steeping, 419.
Flückiger, F. A., on the fluorine salts of antimony, 1.
Fluoantimoniates, on the, 1.
Forbes, D., on the determination of copper and nickel, 276.
Formic acid in the human secretions, 310.
Frankland, Dr. E., on a new series of organic bodies containing metals, 38.
Fraxinine, properties of, 307.
Fremy, E., researches on cobalt, 201; on the sulphurets which are decomposable by water, 261.
Fresenius, R., on a simple means of preventing the formation of incrustations in boilers, 332.
Fuchs, T. R. v., on the structural conditions of iron, 94.
Fungi, acids contained in, 291.
Furfurole, 462.
Fuscobaltia, salts of, 206.
Fusel-oil, examination of, from Indian corn and rye, 281.
Gallic acid, 61.
Galls, examination of Bassorah, 467.
Genth, F. A., on the allotropic modification of oxide of cobalt, 91; on a probably new element, 145.
Gerhardt, M., on the anhydrous organic acids, 136.
Gibbs, Dr. W., on the kakodyle of valerianic acid, 125.
Ginger, essential oil of, 12.
Girard, A., on the action of sulphuretted hydrogen on picric acid, 190; on the action of ammonia on certain metallic arsenites, 229.
Glass containing gold, observations on, 166.
Globuline, 347.
Glycerine, combinations of, with acids, 121, 421; formula for, 384.
Gold, recovery of, from fluids employed for electro-plating and gilding, 354.
Gorgeu, A., on the coloration of the salts of protoxide of manganese, 248.
Grape disease, pentasulphide of calcium a means of preventing and destroying, 414.
Greenshields, T., on improvements in the manufacture of alkali, 438.

Guano, new method of ascertaining the value of, 120.
Gumprecht, M., on a remedy for the stings of bees, 36.
Gunpowder, determination of the quantity of nitrate of potash in, 433.
Hæmatine, 347.
Hassall, A. H., on the frequent occurrence of indigo in human urine, 355.
Heintz, Dr., on mutton fat, 41; on the composition of butter, 441.
Herapath, T. J., on the presence of alumina in boghead coal, and on the employment of the ashes of the latter in the manufacture of alum, 169; on the estimation of iron, cyanogen, hydrocyanic acid, and hydrosulphocyanic acid by volume analysis; and on the quantitative determination of the sulphocyanide of potassium in saliva, 294; on the potato disease, 362, 382.
Higgin, J., on improvements in the manufacture of certain mordants, 440.
Hinterberger, Dr., on the action of the ammoniacal bases upon oil of mustard, 71.
Hirschbrunn, M., on sinapine, 81.
Hodges, Prof., on the gases evolved in steeping flax, 419.
Honey-ant, chemical investigation of the Mexican, 72.
Hops, oil of, 272.
Horny substances, products of decomposition of certain, 346.
Hughes, E. J., on purifying and concentrating the colouring matter of madder, 380.
Hunt, R., on the chemical action of the solar radiations, 415.
Hydrargyromethylium, preparation and constitution of, 40.
Hydrocarbons, fluid, new methods of ascertaining the equivalents of, 365.
Hydrochloric acid, volumetrical determination of, 378.
Hydrocyanic acid, estimation of, by volume analysis, 296.
Hydrogen, on a modification of, 468.
—— and its homologues, on the formation of, 297.
Hydrosulphocyanic acid, estimation of, by volume analysis, 294.
Incrustations in boilers, means of preventing the formation of, 332.
Indigo, determination of the commercial value of, 134; occurrence of, in human urine, 355.
Institution of Civil Engineers, proceedings of the, 158.
Iodine, qualitative and quantitative determination of, 75; separation of, from bromine and chlorine, *ib.*; determination of water in commercial, 118; distribution of, 228; pretended occurrence of, in milk, eggs, and the atmospheric air, 352.
Ipomic acid and salts, 27.
Iridium, new compounds of, 29.
Iron, improvements in the manufacture of, 76; structural conditions of, 94; nitruret of, 229; analysis of pig, 276; on the estimation of, by volume analysis, 294; analysis of cast, 368, 388, 411; separation of, from manganese, 413.
Isatosulphites, constitution of the, 47.
Ivory, improvements in the production of ornamental surfaces on, 59.
Jalap, resin of, 21.
Johnston, Prof., on the origin and decomposition of a mineral called rottenstone, 418; on the properties and composition of the coca leaf, 438.
Jones, Dr. H. B., on the solution of urinary calculi by the aid of electricity, 99.
Joy, C. A., on selenæthyle, 350.
Karsten, Dr., on the reactions upon which the American amalgamation process depends, and on the extraction of silver by means of amalgamation, 141; on the desilverizing of argentiferous lead, 132; on the manufacture of cast steel, 233.
Kawalier, A., on coriander-oil, 16; examination of the leaves of *Arctostaphylos Uva-Ursi*, 61.
Kohl, G., on some double salts of cyanide of mercury, 70.
Köhler, F., on some seleniates and selenites of mercury, 405.
Köller, M., on the products of the decomposition of certain horny substances, 346.
Krieger, G., on the volumetrical determination of manganese, 450.
Kuberth, F., on a product of the action of sulphuric acid on resinized oil of turpentine, 385.
Kühn, O. B., on arsenious acid, its salts, and the arsenio-sulphurets, 364.
Kurrer, W. H., on the applicability of molybdic acid and the molybdates in dyeing and calico-printing, 435.
Lævo-camphoric acid, 450.
Lakes, preparation of, from chloride of antimony, 275.
Lallemand, M., on the composition of essential oil of thyme, 426.
Lampadius, Prof., on the preparation of lakes from chloride of antimony, 275.
Lamy, M., on the saccharine matter of *Protococcus vulgaris*, 200.

Langlois, M., on the action of carbonic acid upon quinine and cinchonine, 470.
Lead, on the desilverizing of argentiferous, 132; new process for determining, 176.
Lecanu, M., on a natural product recently imported from America, 210.
Leditannic acid, constitution of, 13.
Ledum palustre, examination of, 13.
Leers, H. G., researches on quinidine, 161.
Leeshing, F., on the mode of estimating the value of red prussiate of potash, and of testing the strength of bleaching liquors, 139; on the volumetrical determination of copper and oxalic acid, 472.
Lehmann, C. G., on the crystallizable matter of the blood, 442.
Lemercier, M., on photography upon stone, 275.
Leplay, M., on the manufacture of beet-root sugar, 385; on the manufacture of caustic baryta from the carbonate, 387.
Levol, M., on the volumetrical determination of sulphuric and hydrochloric acids, 378.
Leyer, A. C., on the products of the decomposition of certain horny substances, 346.
Lichestearic acid, 292.
Liebig, Prof. J., on cynuric acid, 315; on the separation of nickel from cobalt, 435.
Lime, use of burnt, instead of limestone, as a flux in blast-furnaces, 76; new method of determining the value of chloride of, 217; effect of sulphate of, upon vegetable substances, 437.
Linen, detection of cotton in unbleached, 99.
Lithia, preparation of, from tryphilline, 212.
Lohmeyer, Dr., on the pretended occurrence of iodine in milk, eggs, and the atmospheric air, 352.
Loir, A., on the combinations of the æthylic and methylic hydrosulphuric æthers with metallic chlorides, 361.
Löwig, Prof. C., researches on stannæthyle, 101, 126, 149, 170.
Luca, S. de, on an apparatus for determining carbonic acid, 474.
Luminosity of certain bodies when heated, cause of the, 312.
Luteocobaltia, salts of, 205.
Madder, improvements in purifying and concentrating the colouring matter of, 380.
Magnesium, preparation and properties of, 114; hydrated chloride of, 384.
Manganese, coloration of the salts of protoxide of, 248; separation of, from nickel and zinc, 380; from iron and nickel, 413; new method of determining the commercial value of oxide of, 416; volumetrical determination of, 450.
Margaric acid, researches on, 41.
Margarines, 422.
Martin, A., on a method of obtaining photographic impressions directly upon plates of any description, 213; on an analysis of rain-water, 409.
Maumené, M., on the analysis of oils by means of sulphuric acid, 58.
Mayer, W., on the resin of jalap, 21.
Melsens, M., on the examination of guano, 120.
Mercury, double salts of cyanide of, 70; seleniates and selenites of, 405.
Metals, improvements in the production of ornamental surfaces on, 59; permeability of, to mercury, 89.
Metallic compounds, improvements in the manufacture of, 20.
Methstannæthyle, 110; compounds of, 150.
Methylamine, presence of, in the products accompanying acetone, 409.
Methylenstannæthyle, 112; compounds of, 130.
Milk, composition of, 164.
Moleschott, Dr. J., on the seat of the sugar formation in the animal body, 381.
Molybdic acid, preparation of, 181; new salts of, 348; applicability of, and the molybdates in dyeing and calico-printing, 435.
—— and phosphoric acid, new double salts of, 348.
Montefiore-Levi, E., on the use of burnt lime instead of limestone as a flux in blast-furnaces, 76.
Mordants, improvements in the manufacture of certain, 440.
Morfit, Prof. C., on the analysis of cast iron, 368, 388, 411.
Moride, E., on the determination of iodine, and its separation from bromine and chlorine, 75.
Moritannic acid, formula for, 174.
Moschnin, W., on caprylic alcohol, 430.
Müller, H., on the preparation of lithia from triphylline, 212; on palladamine, 241, 263.
Mustard, action of the ammoniacal bases upon oil of, 71.
Mutton-fat, researches on, 41.
Newton, W E., on the manufacture of carbonate of soda, 359.

Nickel, determination of, in quantitative analysis, 276; separation of, from copper, 379; from manganese and cobalt, 380, 435.
Nicklès, J., on the permeability of metals to mercury, 89; on improvements in the manufacture of sugar, 385.
Nitrate of potash, improvements in the manufacture of, 20.
Nitrocinnamic acid, anhydrous, 212.
Nitrogen, formation of almost pure protoxide of, 250.
Nitroprusside of sodium, preparation of, 271.
Oil of ginger, 12; of roses, fabrication of, in the Balkan, 98; of cummin, analysis of, 226; of hops, on the, 272; of lemon and turpentine, on the ozonization of the, 331; of thyme, on the composition of essential, 426.
Oils, compounds formed by some essential, with the alkaline bisulphites, 46; analysis of, by means of sulphuric acid, 58.
Oleine, 423.
Osann, G., on a modification of hydrogen, 468.
Othyle, 138.
Overbeck, A., on the preparation of nitroprusside of sodium, 271.
Oxalic acid, determination of, 472.
Oxycobaltia, salts of, 203.
Oxylizaric acid, researches on, 316.
Palladamine, researches on, 241, 263.
Palladdiamine and compounds, 263.
Papier-maché, substitute for, 439.
Papousek, A., on essential oil of ginger, 12.
Paracitric acid and paracitrates, 32.
Paraffine, manufacture of, 476.
Pasteur, L., on quinidine, 123; on the conversion of tartaric acid into racemic acid, 292; on the alkaloids of the cinchonas, 321; on the transformation of tartaric acid into racemic acid, the discovery of inactive tartaric acid, and a new method of separating racemic acid into dextro- and lævo-tartaric acids, 401.
Pearsall, J., on crystals from the seacoast of Africa, 418.
Pelargonic acid, researches on anhydrous, 88; combination of, with deutoxide of nitrogen, 123.
Pelargonic æther, preparation of, 144.
Penot, Dr., on a new method for determining the value of chloride of lime, 217.
Personne, J., on the fermentation of citric acid, 147.
Phosphoric acid, determination of, 17.
Phosphoric and molybdic acid, new double salts of, 348.
Phosphorus, action of, upon certain classes of salts, 329; on the so-called amorphous, 447.
Photographic impressions, method of obtaining, directly upon plates of any description, 213.
Photography upon stone, 275.
Phycite, analysis of, 200.
Physaline, preparation and composition of, 15.
Picramic acid, preparation and constitution of, 191.
Picric acid, action of sulphuretted hydrogen on, 190; employment of, for distinguishing vegetable and animal fibres in stuffs, 320.
Pohl, Dr. J. J., on the employment of picric acid for distinguishing vegetable and animal fibres in stuffs, 320; on the constituents of fat, 383.
Poisons, new method of analysis for the organic, 215.
Potash, preparation of pure hydrate of, 429.
Potato disease, remarks on the, 362, 382.
Price, Dr. A. P., on the employment of pentasulphide of calcium as a means of preventing and destroying the grape-disease, 414; on a new method for determining the commercial value of oxide of manganese, 416; on a new method for determining the amount of available chlorine contained in hypochlorites of lime, soda or potash, 419.
Propionic alcohol, 428.
Propylamine, new double salt of, 94.
Protococcus vulgaris, on some constituents of, 200.
Prussiate of potash, new mode of estimating the value of red, 139.
Purpurine, constitution of, 316.
Puttfarcken, A., on the so-called amorphous phosphorus, 447.
Queen-bee, examination of the food of the, 91.
Quinicine, preparation and properties of, 322.
Quinidine, researches on, 123, 161, 322; action of heat upon, 323.
Quinine, adulteration of the citrate of iron and, 269; action of carbonic acid upon, 470.
Racemic acid, new method of separating, into dextro- and lævo-tartaric acids, 401.
Rain-water, analysis of, 409.
Realgar, insolubility of native, in carbonate of ammonia, 252.
Reckenschuss, M., on new double salts of æthylamine and propylamine, 94.

Red fire, 388.
Reynoso, A., on the action of water upon various bodies at a high temperature and under strong pressure, 189.
Rhodeoretine, preparation and composition of, 21; products of decomposition of, 24.
Rhodeoretinic acid and salts, 23.
Rhodeoretinolic acid and salts, 24.
Rhododendron ferrugineum, examination of the leaves of, 44.
Rhodotannic acid, 44; rhodoxanthine, 45.
Riche, A., investigation of stannæthyle, 292.
Rieffel, M., on the chemical compounds of copper and tin, and their mixtures with one another, 448.
Robierre, A., on the composition of beet-root, 154.
Rochleder, F., on *Ledum palustre*, 13; on the chemistry of the plants of the family *Ericineæ*, 187; on some bitter principles, 301.
Rose, H., on the influence of water upon boracic acid in borates, 65, 194, 214, 232, 270, 404; on the isomeric combinations of sulphur and antimony, 290; on the reduction of arsenic and antimony by means of cyanide of potassium, 399.
Roseocobaltia, salts of, 208.
Rotten-stone, origin and composition of, 418.
Royal Institution, proceedings of the, 136, 297.
Royal Society, proceedings of the, 38, 99, 355.
Rutic acid, use of, in dyeing, 222.
Sal-ammoniac, method of getting rid of, in analysis, 115.
Saline compounds, on improvements in the manufacture of, 20.
Saliva, quantitative determination of the sulphocyanide of potassium in, 294.
Sandrock, B., on the preparation of the tannic acids, 199.
Schaffner, Max., on an apparatus for the determination of carbonic acid, 37.
Schiel, Dr. T., on the separation of manganese from iron and nickel, 413.
Schmidt, Dr. E., on the use of burnt lime instead of limestone as a flux in blast-furnaces, 76.
Schrötter, A., on the cause of the luminosity of certain bodies when heated, 312.
Schwartz, Dr. H., on new processes for determining copper, lead and sulphuric acid, 176.
Schwartz, R., on *Ledum palustre*, 13; examination of the leaves of *Rhododendron ferrugineum*, 44; on some bitter principles, 301.
Sebacic acid, on an apparently new mode of formation of, 155; researches on, 324.
Sebine, 122, 425.
Selenæthyle, researches on, 350.
Seleniates and selenites of mercury, 405.
Seminaphthalidine, 32.
Sigwart, Prof., on the distribution of iodine, 228.
Silver, new alloy of, 15; extraction of, by means of amalgamation, 141; recovery of, from the fluids employed for electro-plating and gilding, 354.
Sinæthylamine, preparation and constitution of, 71.
Sinapic acid and salts, 83.
Sinapine, researches on, 81; preparation and constitution of, 86.
Sinkaline, preparation and composition of, 84.
Skinner, T., on improvements in producing ornamental surfaces on metal, ivory or bone, 59.
Skoblikoff, M., on some new compounds of iridium, 29.
Slater, J. W., on the action of phosphorus, sulphur, arsenic, and antimony upon certain classes of salts, 329.
Smith, Dr. J. L., on a method of getting rid of sal-ammoniac in analysis, 115; on the formation of almost pure protoxide of nitrogen by the action of nitric acid on sal-ammoniac, 250; on the quantitative determination of the alkalies in the siliceous minerals not soluble in acids, 252, 333; on the supposed new element thalia, 353.
Soap, process for determining the value of, 55.
Soaps, researches on, 115.
Soda, improvements in the manufacture of, 20, 359.
Sodium, preparation of nitro-prusside of, 271.
Solar radiations, on the chemical action of the, 415.
Spirgatis, H., on the analysis of copper and zinc alloys, 259.
Splittgerber, M., on glass containing gold, 166.
Stædeler, Prof. G., chemical examination of acetone, 341.
Stanmethyle, investigation of, 292.
Stannæthyle, researches on, 101, 126, 149, 170.
Stannæthylium, preparation and constitution of, 38.
Stearines, on the, 422.
Steel, manufacture of cast, 233.

Stein, Prof. W., on a new dye-stuff, 221.
Sting of bees, remedy for the, 36.
Strychnine, new salts of, 70.
Sugar, improvements in the manufacture of, 385; formation of, in the animal body, 381; products of the dry distillation of, 461.
Sulphamylate of lime, action of ammonia upon, 326.
Sulphocaprylates, 432.
Sulphotritylic acid, 429.
Sulphur, action of, upon certain classes of salts, 329.
—— and antimony, on the isomeric combinations of, 290.
Sulphurets, observations on the, which are decomposable by water, 261.
Sulphuric acid, new process for determining, 176, 378.
Swoboda, A., on some double salts of cyanide of mercury, 70.
Tannic acids, preparation of the, 199; on the constitution of the, 310.
Tartaric acid, conversion of, into racemic acid, 292, 401; on the discovery of inactive, 401.
Telluræthyle, new compounds of, 49.
Thalia, on the supposed new element, 353.
Thiacetouine, 344.
Thiosinæthylamine, 71.
Thymole, preparation and properties of, 426.
Tin and copper, compounds of, 448.
Titanium, phosphuret of, 427.
Trityle, hydrate of, 428.
Tritylosulphocarbonic acid, 429.
Turpentine, on a product of the action of sulphuric acid on, 385.
Tyrosine, 347.
Uchatins, F., on the determination of the quantity of nitrate of potash contained in gunpowder, 433.
Urea, on the production of, 287.
Urinary calculi, solution of, in dilute saline fluids, 99.
Urine, presence of formic acid in, 311; frequent occurrence of indigo in, 355.
Valeranilide, preparation and properties of, 54.
Valerianic acid, anhydrous, 52; kakodyle of, 125.
Valerines, 122, 424.
Vernois, M., on the composition of milk, 164.
Völckel, M., on the manufacture of pure acetic acid, 96; on oil of cummin, 226; on the products of the dry distillation of organic bodies, 461.
Wagner, Dr. R., on the preparation of crude pelargonate of oxide of æthyle, 144; on an apparently new mode of formation of sebacic acid, and on the constitution of the acids of the group $(C^n H^{n-2})+O^3$, 155; on the formula for moritannic acid, 174; on the oil of hops, 272.
Warren, P., on a substitute for papier-maché, 439.
Water, influence of, upon boracic acid in the borates, 65, 404; action of, upon various bodies at a high temperature and under strong pressure, 189.
Wetherill, Dr. C. M., on the Mexican honey-ant, 72; on the food of the queen-bee, 91; examination of fusel-oil from Indian corn and rye, 281.
Williams, C. G., on the insolubility of native realgar in carbonate of ammonia, 252; on the adulteration of the citrate of iron and quinine of commerce, 269; on the ozonization of the oils of lemon and turpentine, 331; on a process for ascertaining the equivalents of some fluid hydrocarbons, 365; on the presence of methylamine in the products accompanying acetone, 409.
Williamson, Prof., on Gerhardt's discovery of anhydrous organic acids, 136.
Winckler, F. L., on the chemical constitution of wines, 32.
Wines, on the constitution of, 32.
Wittstein, M., on the determination of the commercial value of indigo, 134.
Wöhler, Prof., on new compounds of telluræthyle, 49.; on the preparation of pure hydrate of potash, 429.
Wurtz, A., on the products of decomposition of the cyanic æthers, 407.
Zenker, Dr. F. E., on new double salts of phosphoric and molybdic acid, 348.
Zimmermann, O., on the detection of cotton in unbleached linen, 99.
Zinc, separation of, from copper 79; from manganese and cobalt, 380.
—— and copper alloys, analysis of, 259.
Zincmethylium, preparation and constitution of, 39.
Zinin, N., on azobenzide and seminaphthalidine, 32.

END OF VOLUME XI.

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